LIBRARY

VOL. XV. 3. OCTOBER, 1861.

THE QUARTERLY JOURNAL OF THE CHEMICAL SOCIETY.

Committee of Publication.

W. DE LA RUE, PH.D., F.R.S. | A. W. HOFMANN, LL.D., F.R.S.
E. FRANKLAND, PH.D., F.R.S. | A. W. WILLIAMSON, PH.D., F.R.S.

N° LV.

LONDON:

HIPPOLYTE BAILLIERE, 219, REGENT STREET,

BAILLIERE BROTHERS, 440, BROADWAY, NEW YORK.

PARIS: J. B. BAILLIERE, LIBRAIRE, RUE HAUTEFEUILLE.

MADRID: BAILLY BAILLIERE, LIBRAIRE, CALLE DEL PRINCIPE.

T. T. BAILLIERE, COLLINS STREET EAST, MELBOURNE.

1861.

Price Three Shillings.

LONDON: PRINTED BY HARRISON AND SONS, ST. MARTIN'S LANE, W. C.

CHEMICAL SOCIETY.

Officers and Council.

Elected March 30, 1861.

PRESIDENT.

A. W. HOFMANN, LL.D., F.R.S.

VICE-PRESIDENTS,

WHO HAVE FILLED THE OFFICE OF PRESIDENT.

W. T. BRANDE, F.R.S.
B. C. BRODIE, F.R.S.
C. G. B. DAUBENY, M.D., F.R.S.
THOMAS GRAHAM, F.R.S.
W. A. MILLER, M.D., F.R.S.
LYON PLAYFAIR, PH.D., C.B., F.R.S.
COLONEL PHILIP YORKE, F.R.S.

VICE-PRESIDENTS.

H. BENCE JONES, M.D., F.R.S.
ROBERT PORRETT, F.R.S.
ALFRED SMEE, F.R.S.
A. W. WILLIAMSON, PH.D., F.R.S.

SECRETARIES.

THEOPHILUS REDWOOD, PH.D.
WILLIAM ODLING, M.B., F.R.S.

FOREIGN SECRETARY.

E. FRANKLAND, PH.D., F.R.S.

TREASURER.

WARREN DE LA RUE, PH.D., F.R.S.

OTHER MEMBERS OF THE COUNCIL.

THOMAS ANDREWS, M.D., F.R.S.
WILLIAM FRANCIS, PH.D., F.L.S.
J. H. GLADSTONE, PH.D., F.R.S.
G. D. LONGSTAFF, M.D.
W. MARCET, M.D., F.R.S.
JOHN MERCER, F.R.S.
A. R. NORMANDY, ESQ.
W. H. PERKIN, ESQ.
H. E. ROSCOE, PH.D.
EDWARD SCHUNCK, PH.D
JOHN STENHOUSE, LL.D., F.R.S.

EDITOR.

HENRY WATTS, B.A., F.C.S.

COLLECTOR.

MR. THOMAS WEST, BURLINGTON HOUSE.

Considerable difficulties were encountered in the endeavours properly to balance these conditions, when attempts were made, which will presently be mentioned, to apply the mixture in question to the ignition of several charges in circuit. The increase in the resistance of the current, consequent on the introduction of more than one interruption in the metallic circuit, necessitated an increase in the conducting power of the mixture, which it was difficult to attain, unless at a considerable sacrifice of the sensitiveness of the composition. It was consequently found that, when the proper conditions had been attained for ensuring the passage of the current through several (five or six) fuzes in circuit, the absolute certainty of the fuze, when applied in this manner, had been sacrificed. Thus, out of several fuzes tried together, which had been most carefully prepared, so as to be, as far as possible, perfectly alike, the current would ignite a few, passing through the others without affecting them; and would thus point to minute differences in the conducting powers and sensitiveness of different portions of one and the same quantity of the mixture, which, it is almost needless to observe, was prepared in such a way as to ensure the greatest possible uniformity.

By a large number of careful experiments, the proportions of ingredients were at length determined, which furnished a mixture possessed of high conducting power, attainable without detriment to the sensitiveness (ready explosiveness) of the material. The perfect certainty of its action, when applied in the fuze, to the explosion of a single charge by means of magneto-electric machines, has been proved by the ignition of at least 5000 fuzes without failure. A large number of these have been fired by means of the smaller machines already referred to.

The fuzes contrived by me for use with magneto-electric apparatus are of two kinds, the one being adapted for mining purposes and the other for firing cannon. The fuze for mining purposes (fig. 4) consists of,—

a. A head for receiving the wires which connect the fuze with the magnet and the earth;

b. Of the insulated wires, with the terminals of which the priming material is in close contact;

c. Of a small cartridge or charge of powder, enclosing the terminals, upon which the sensitive composition rests.

The wooden fuze-head contains three perforations (*a a*, *b b*, *c c*, fig. 5); the one, passing downwards through the centre, receives

Fig. 4.

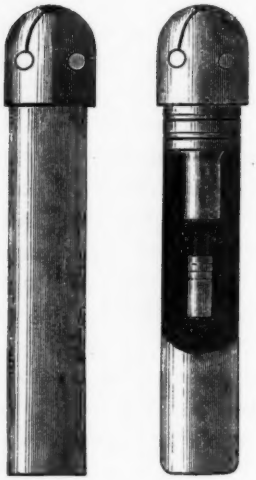
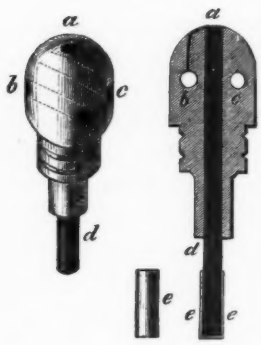


Fig. 5.



about two inches of double insulated wire, *d*.* The other two perforations, which are parallel to each other on each side of the central one, and at right angles to it, serve for the reception of the circuit-wires. The arrangement for securing the connection of these with the insulated wires in the fuzes is as follows:—

The piece of double covered wire above referred to, is originally of a sufficient length to allow of the gutta percha being removed from about one and a-half inches of the wires. These bare ends of the fine wires, which are made to protrude from the top of the fuze-head (*a*, fig. 5), are then pressed into slight grooves in the wood provided for their protection, and the extremity of each is passed into one of the horizontal perforations in the head, in which position it is afterwards fixed by the introduction into the hole of a tightly-fitting piece of copper tube, so that the wire is firmly wedged between the wood and the exterior of this tube, and is thus at the same time brought into close contact with a comparatively large surface of metal. It will be seen that it is only necessary to fix one of the circuit-wires into each of these tubes in

* This double covered wire consists of two copper wires of 0·022 inch diameter, enclosed side by side, at a distance of $\frac{1}{16}$ inch apart, in a coating of gutta percha of $\frac{1}{8}$ inch diameter. It has been prepared by the Gutta Percha Company for this particular purpose in considerable lengths (300 yards), from which the pieces of requisite length are cut off as required. The insulation of the two wires has been found perfect throughout the whole length manufactured at one time.

the opposite sides of the fuze-head, in order to ensure a sufficient and perfectly distinct connection of each one of them with one of the insulated wires in the fuze.

The phosphide of copper fuze for firing cannon (fig. 6) differs somewhat in construction from the mining fuze. The head is somewhat longer, and of such a form that the double-covered wires are completely enclosed in it, the lower extremity of its central perforation still remaining free to receive the top of the quill- or copper-tube, which is charged with gunpowder in the same manner as the ordinary tube-arrangement for firing cannon.

Fig. 6.

Numerous experiments made with the aid of the detonating mixture with which these fuzes were primed, established the fact that the current obtained by means even of a very powerful magneto-electric machine, when applied to the ignition of several charges arranged *in succession* in one circuit, is very limited in its powers. In illustration of this, it may be stated that, on trial being made of twenty-one consecutive sets of four charges, eighteen of the sets were perfectly discharged, but in the other three sets, only two or three of the charges were ignited. Out of five sets, of five charges each, only two sets were completely discharged; and in several attempts made to ignite six fuzes in one circuit, only four were fired in each case. In all these experiments, when charges had escaped ignition, the current had passed through the sensitive composition without firing it. When the discharged fuzes were removed, and the remaining ones properly connected, they were all fired. It has been already stated, that no beneficial effects were attained by modifying the proportions of ingredients in the priming composition, so as to diminish or increase its conducting power. Three charges might, therefore, be considered the largest number that could be ignited *with certainty* by means of a powerful electro-magnetic machine, when they were arranged in succession, in simple circuit.

The plan originally suggested by M. Savare, of arranging the charges in divided circuits was next tried, and furnished far more successful results. The simultaneous ignition of twenty-five charges, arranged as shown in fig. 2, was repeatedly

effected; and forty charges were similarly exploded on several occasions. These results were all obtained with the large magnet constructed by Henley, the current being established by rapidly separating the armature from the poles by means of a lever. By a simple arrangement for shifting the connection of the main wire with the exploded charges from them to a second series, similarly arranged, twenty-five were almost simultaneously ignited on allowing the armature to return to the poles of the magnet. It was found, moreover, that the same number could be fired by means of this magnet, even if two folds of thick brown paper were interposed between the poles and the armature, so that, on depression of the lever, the armature had no longer to be forcibly detached, but simply to be removed from the magnet. The success of these results led to trials of magneto-electric machines of comparatively small size, with revolving armatures. In the employment of these machines, it was of course not expected that any single induced current obtained from them should distribute itself among a number of fuzes placed in divided circuit, as is the case with the comparatively much more powerful current obtained with the large magnet, but it was hoped that the very rapid succession of currents furnished by them would produce a very similar result, by distributing themselves over the different branches of the circuit with which the fuzes were connected, and that the ignition of the whole of the fuzes, though it could not be so positively instantaneous as when the one current was discharging the entire number, might yet be effected with such rapidity as practically to amount to a simultaneous discharge.

The results obtained fully confirmed these expectations. With a small horse-shoe magnet, 7 inches in length, 1 inch in breadth, and $1\frac{3}{4}$ inches in thickness, provided with a revolving armature and multiplying wheels, by which great rapidity of motion could be attained, twenty-five charges were fired; the effect of the discharge on the ear was, however, not like that of one single explosion, as was the case in the former experiments, but like that of an exceedingly rapid volley, in which the explosion of any single charge could not be distinguished. Still more favourable results were obtained with a very compact arrangement consisting of six small magnets, to the poles of which were fixed soft iron bars, surrounded by coils of insulated wire. The coils of all the magnets were united together so as to form, with the external conducting wire and the earth, a single circuit. An axis carried six soft iron

armatures in succession before each of the coils. By this arrangement, two advantages were gained; all the magnets simultaneously charged the wire and produced the effect of a single magnet of more than six times the dimensions, and, at the same time, six shocks or currents were generated during a single revolution of the axis, so that, when aided by a multiplying motion applied to the axis, a very rapid succession of powerful currents was produced. A single large magnet with a rotating armature could not be made to produce the same succession of currents without the application of considerable mechanical power. Another peculiarity of this apparatus was that the coils were stationary, and the soft iron armatures alone were in motion: by this disposition, the circuit was never broken during the action of the machine. In the usual magneto-electric machines with rotating armatures, the circuit is necessarily broken twice during every revolution; and this frequently gives rise to irregularities in the production of the currents. By the construction adopted, the currents can never fail to traverse the circuit.

By means of this apparatus, twenty-five charges were frequently fired in divided circuit, with such rapidity that the effect on the ear was as of one explosion, only of slightly longer duration than when the large magnet was employed.

On some occasions, when a slight difference was made in the velocity with which the apparatus was worked, an interval could be distinctly noted between the first and last discharge, but even in those instances, the effect could not be considered as otherwise than a practically simultaneous discharge. Some sets of fifty charges in divided circuit were also ignited by means of this apparatus; but in those instances the interval between the first and the last discharge was naturally longer, being about the same as that observed when twenty-five charges were fired by means of the small magnet above referred to.

The system of firing charges by means of magneto-electricity, with the aid of the phosphide of copper fuze, having been thus far successfully developed, a series of experiments was instituted at Chatham, for the purpose of thoroughly testing its certainty and applicability in the field, and subsequently for ascertaining the extent to which it admitted of application to the explosion of submarine charges. These experiments extended over a period of six months, and were performed under various conditions of weather.

It will readily be understood that the best and most simple method of connecting the fuzes, enclosed in the charges, with the branch-wires and the earth, of arranging the experimental charges for explosion, and of carrying out the various small but essential details involved in the operations, were only gradually arrived at; and that, consequently, in many of the first experiments, which were only partially successful, the failures were traced to causes unconnected with the efficiency of the magneto-electric apparatus, or the fuze. It would be superfluous in this memoir to enter into details with regard to those preliminary experiments, however important they were at the period of the investigation; the description of the operations at Chatham will therefore be confined to those which were carried on according to the plan which was ultimately proved to be most efficient. The magneto-electric apparatus employed in all the field experiments was Mr. Wheatstone's arrangement of six small magnets, just now described, the whole apparatus having been enclosed in a box, so that the only exposed portions were the binding screws for the attachment of the wires, a handle for setting the armatures in motion, and a key, by the depression of which, at a given signal, the circuit could be completed.

To employ the instrument at any moment, only the following operations were necessary; the insulated wire and the copper wire passing to the earth were fixed to the apparatus by means of binding screws: the instrument was raised from the ground by being placed on its packing case; at that height, a man could operate with it when in a kneeling posture. At the signal "Ready," the handle was turned with one hand, so as to cause the armatures to revolve with the greatest possible velocity, whilst the other hand was pressed against one corner of the instrument close to the key, so as to steady the box and to be ready, at the signal "Fire," to depress the key with the thumb.

The connection of the instrument with the earth was effected as follows: a moderately clean spade was selected from among those used by the men in digging holes for the charges. One end of a piece of stout copper wire was placed under the edge of the spade, so that, when the latter was firmly forced into the ground, the wire was pressed by the earth on both sides against the iron surface. The protruding wire was wound once or twice round the bottom of the spade handle, and then attached to the binding screw of the magnet.

The gutta-percha-covered wire used in the experiments having

been in occasional service at Chatham for some years, the coating had sustained some injury in two or three places. Such defects were protected from possible contact with the earth by means of waterproof cloth or sheet india-rubber. The total length of wire used was 881 yards, of which 600 were extended, lying along the ground.

To the extremity of the covered wire a number (from 12 to 25) of pieces of similar insulated wire, varying in length between three and six yards, and serving to connect it with the individual charges, were attached in the following manner; about six inches of the extremity of the main wire and of each of the branch wires were laid bare and cleansed; the end of the former was then surrounded with those of the latter (placed in an opposite direction) and the whole tightly twisted together by means of pliers, so as to be brought thoroughly in contact with each other and with the main wire. The twisted wires were then bound round with moderately fine copper wire, which was made to bring every portion of the exterior of the bundle into connection. The joint was made rigid with pieces of stick tied against it and the whole securely enveloped in a piece of waterproof cloth or canvas, to protect it from damp and contact with the earth.

These connections, though of a very rough description and most readily prepared by any soldier, were thoroughly effectual. No instance occurred, in the whole of the experiments, of the failure of a charge, which could be attributed to an imperfect connection of its branch wire with the main wire.

The following was the method adopted for connecting the fuzes with their respective branch wires and with the earth.

The fuzes, as they were manufactured, were always fitted with two pieces of covered wire twisted together (Fig. 7), which were tightly fixed into their proper positions by forcing a short pin of copper wire into the holes of the fuze-head. They were thus ready for insertion into the bag or other receptacle containing the charge

Fig. 7.

of gunpowder, the ends of the covered wires protruding from the opening of the latter to a convenient distance for effecting the

junction with the branch- and earth-wires. The extremities of one of the fuze-wires and of a branch wire (from both of which the gutta-percha was removed to a distance of about two inches) were connected by hooking them firmly one in the other with pliers (in

Fig. 8.

the manner shown in Fig. 8). A piece of fine copper binding wire was then twisted over the whole of the connection, and the joint was finally enclosed in a small wrapping of oiled canvas, in a manner similar to that adopted at the principal junction with the main wire.

The extremity of the other fuze-wire was attached to an uncovered copper wire, of sufficient length to bring the whole of the charges into connection with each other in this manner. The wire was fixed in a convenient position by being twisted round short stakes or pickets driven into the ground, and its extremities were buried in the earth, being attached either to spades, as already described, or to zinc plates about eight inches square.

The very rapid and comparatively rough manner in which these various connections were made (the tedious operation of brightening every metallic connection, so essential with the employment of the voltaic battery, being dispensed with), and their universally efficient character, were particularly commended by the officers and men who witnessed and assisted in the experiments. With reference to the earth-connections, the employment of large metallic surfaces was proved, by repeated experiments at Chatham and Woolwich, to be superfluous. The simple insertion into the ground of the uncovered extremity of the fuze-wires was found to afford a perfectly sufficient connection for ensuring the ignition of charges. The plan above described of connecting together the whole of the charges was, however, adopted as being undoubtedly the mode of proceeding least liable to accidental derangement.

The largest number of charges which it was attempted to fire at once at Chatham was twenty-five. The ignition of twelve charges was repeatedly effected, and with such rapidity as to have the practical effect of a simultaneous discharge of the whole. With twenty-five charges, the interval between the first and last discharge was very decided; it was considered, however, that even

the ignition of the twenty-five charges (at a distance of 600 yards from the magnet, and with the employment of 881 yards of covered wire, and in addition, about 100 yards in the form of branch-wires) was effected with sufficient rapidity to allow of that number being employed in cases where a simultaneous discharge was required.

It need scarcely be stated that in dealing with electricity of induction, defects in the insulation of the main and branch wires had to be very carefully guarded against. Several failures in the first experiments were eventually traced to some defect of that kind. An instance even occurred, before the proper method of protecting the connections of the charges with the insulated wires was adopted, in which the deposition of moisture upon the gutta-percha-covered wire, near the charge, prevented the ignition of the latter, by forming a connecting link between the extremity of this wire, where it was exposed and attached to the fuze, and the uncovered wire leading to the earth, in consequence of the two wires being in contact at a distance of several inches from the fuze. It is therefore always a preliminary precaution of primary importance, that the insulating covering of the wire to be employed be carefully inspected, while the latter is being laid out for use, and that any imperfections be protected from possible contact with the earth, or from the access of moisture; a result easily attainable by the application of some waterproof envelope to the injured portion.

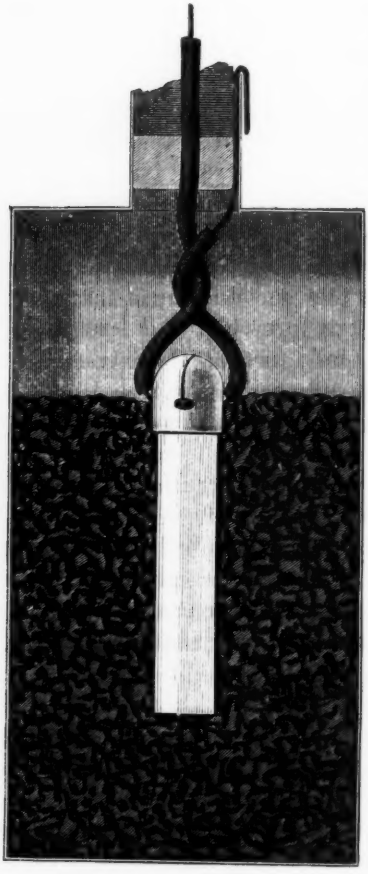
The experiments instituted at Chatham with the object of applying the magneto-electric current to the ignition of *submarine* charges were attended with greater difficulties than those which served to test the system in its application to land-operations; nevertheless, the results ultimately attained were also of a character to lead to definite and favourable conclusions.

The method of establishing the connections of a charge with the wire and the earth differed naturally in some respects from the mode of proceeding already described. The charges of powder were contained in canisters of block tin carefully soldered so as to be watertight.* The fuze, with two wires attached as before, the one a few inches longer than the other, was inserted into the charge, and fixed in its proper position in the canister by means of a

* Any vessels of this material, such as turpentine cans, may be employed, provided they be perfectly coated inside with marine glue, or some other description of varnish.

loose fitting bung (see Fig. 9) pushed a little distance into the neck, and cut out on one side, so as to admit of the passage of the longer insulated wire, while the bare part of the shorter wire was firmly pressed by the cork against the inside of the neck. The latter was then completely filled up with melted gutta-percha, and the extremity of the short uncovered wire was bent back over its side, so as to be in close contact with the metal surface. In this manner, the enclosed fuze was brought into good metallic connection with the wet earth, or water, by which the canister was surrounded.

Fig. 9.



The insulated wire, projecting from the mouth of the canister, was connected with one of the branch wires in the manner already described; but in order thoroughly to protect the connection from the water, in which it would become immersed, a piece of vulcanized India-rubber tubing, of suitable length, and a tin-tube, rather longer and wider than the latter, were slipped on to the branch-wire before it was joined to the fuze-wire, and, when the junction had been effected, the India-rubber tube was pulled over it, and tied very firmly at both ends on to the gutta-percha covering of the wires. (Fig. 10).

Fig. 10.

A small quantity of a cement (consisting of bees-wax and turpentine) was rubbed in between the latter and the ends of the India-rubber tube, so as thoroughly to ensure the exclusion of water, and finally the tin-tube was pulled over the joint, and fixed (by compressing the ends) for the purpose of imparting rigidity to the junction, and thus protecting it from injury by any sudden twist or strain. By these arrangements, when carried out with moderate care, the perfect exclusion of water from the charge and from its connection with the branch wire was effected.

The first trials of these charges were made in a shallow canal with a mud bottom, and from which at the time of experiment the water was receding so rapidly, that before the whole of the charges had been immersed, several of them were exposed to view, being partly imbedded in the mud. Twenty-five charges were arranged, of which thirteen were exploded, though less rapidly than in the experiments on land. On the next occasion, when twenty-five charges were entirely surrounded by water (simply resting upon the firm bed of a pond of some depth), only four of the charges were exploded. Several other attempts were made to fire a smaller number of (ten and five) charges similarly immersed, but in every instance only four were ignited. A careful examination into the cause of the invariable explosion of so comparatively limited a number of charges under water, led to the following explanation:

It will be remembered that the explosion of numerous charges in a divided circuit by the magneto-electric apparatus with revolving armatures is effected by the action of an exceedingly rapid succession of currents. The rapidity with which they follow each other, however great, cannot equal that with which the terminals of a fuze, enclosed, in a small charge, under water, come into contact with the latter after the explosion. The instant this occurs, a complete circuit is established through the water, and any further action of the current is at once arrested. By the time, therefore, that four charges had been ignited in extremely rapid succession, so as to be apparently exploded at once, a sufficient interval of time had in reality elapsed to allow the water to re-occupy the space filled for a brief period by the gaseous products of the first explosion, and thus to rush in upon, and complete the circuit with, the terminals of the fuze. It appears probable that, with the employment of larger charges of powder (about eight ounces was the quantity exploded in each charge) when the

volume of water displaced by the explosion would be more considerable, a great number of charges would be exploded before the circuit could be completed by the water. No opportunity occurred during the experiments of ascertaining this by actual trial.

The instances, however, in which it is indispensably necessary that a number of charges should be exploded together, suspended in water, or simply resting on the ground below, and being in immediate contact on almost all sides with water, appear to be of exceptional occurrence. Submarine charges are generally so arranged as to be partially or completely surrounded by the objects upon which the force of the exploding charge is to be exerted, and they are even frequently firmly fixed in their position by being partly or wholly embedded in sand, mud, or some similar material. In such cases, the resistance to be overcome by the explosion is greater than if, under conditions otherwise similar, the charges were simply in direct contact with the water, and hence the interval is increased which must elapse before the water can complete the circuit.

The results of some experiments made at Chatham appear to show that, under such circumstances, the number of charges ignited at one time by the magneto-electric apparatus must be greater than if they were simply immersed in water. One experiment has already been mentioned, in which thirteen charges out of twenty-five were exploded at one time, most of them being imbedded in mud. On another occasion ten charges were placed in small pits filled with water, the canisters being covered in with mud beneath the latter. Nine of the charges were fired; the branch wire of the tenth was accidentally severed at the moment of the explosion, from its lying across one of the pits.

A careful consideration of the results furnished by these and other similar experiments, on the application of magneto-electricity to the explosion of charges, led to the following conclusions:

The explosion of a single charge of powder by means of the phosphide of copper fuze and a magneto-electric apparatus (even of the smallest size generally manufactured) is absolutely certain.

With the employment of a magneto-electric apparatus similar to that used in the Chatham experiments, and termed by Mr. Wheatstone the "magnetic exploder," the ignition at one time, of fuzes varying in number from two to twenty-five, is certain, provided these fuzes are arranged in the branches of a divided

circuit in the manner described. To attain this result, it is only necessary to employ a single wire, insulated by a coating of gutta-percha or India-rubber, and simple metallic connections of the apparatus and the charge with the earth. The explosion of from twelve to twenty-five charges may be effected in the above manner, at a distance of at least 600 yards from the apparatus, with a rapidity which in its results will in all probability have the practical effect of a simultaneous discharge. This statement refers only to charges on land. The number of submarine charges which can be exploded with certainty at one time by means of the magnetic exploder appears more limited; but if such charges are entirely or partially embedded in sand, mud, or other dense materials, from two to ten may be fired with certainty. By the employment of separate wires, leading from the instrument to each charge, or by adopting a rheotomic arrangement for effecting the discharge, there is little doubt, however, that the results obtained with the magnetic exploder in submarine operations would be quite equal to those definitely established in the ignition of charges on land.

The only precaution to which it is necessary to attend, in order to ensure uniform success in the application of the magnet, are the proper insulation throughout of the main wire and branch wires leading from the instrument to the charges, and the thorough protection of all connections of wires from the access of moisture.

The system of firing charges by magneto-electricity possesses important advantages over the application of the voltaic battery to that purpose, the principal of which are as follows:

The magnetic exploder is at any time ready for immediate employment; it is easily transported by hand, being of small dimensions and weight; it is not liable to injury or derangement provided the most ordinary care be applied to its preservation and transport; it may be employed for many years without suffering any important diminution of its power; and, as all arrangements in connection with the instrument are mechanical, any injury which they may sustain can be repaired by ordinary workmen.

The magnet-fuze is more certain than any fuze-arrangement applied with the voltaic battery, and as safe as any arrangement employed for igniting gunpowder by friction or percussion. It may be preserved for a great length of time in any climate, and will bear very rough treatment without chance of injury.

The implements and materials required for carrying on opera-

tions with the magnet, in addition to the instrument, the wire and the fuzes, are very few in number, inexpensive, and easily replaceable; they occupy but little space, and require no more care in their transport than ordinary artisan's tools.

All the operations necessary in the employment of the magnet (the connection of the fuzes with the instrument, their introduction into the charges, and the explosion of these), are of the simplest possible character, and can therefore be performed by any person of ordinary intelligence.

It can be confidently affirmed that the general certainty of the magneto-electric arrangement is decidedly greater than that of voltaic batteries, and that the necessity of ensuring a proper insulation of wires and connections, though it may be regarded in the light of a difficulty by those accustomed to carry on operations with the voltaic current, is in reality a condition which may be fulfilled readily and with certainty by the use of very simple means and precautions.

There is little question that, with battery-power of great magnitude, and with the successful fulfilment of the numerous indispensable conditions and precautions (which long experience has shown to be involved in considerable uncertainty), it is possible to fire at one time a very much larger number of charges than those which have been quoted as the greatest task to be accomplished with certainty by the apparatus proposed for general use. It has, however, been stated by high military authorities on these subjects, that the instances in which it is required to fire more than from twelve to twenty charges at one time are quite exceptional, and that indeed, twelve may be considered as the greatest number of charges which it may be necessary to apply in all general operations.

In special cases, such as the destruction of very massive works, where it would be advantageous to apply the force of exploding gunpowder simultaneously to a very large number of different places, the employment of arrangements of a special character is always admissible. In such circumstances, there is no question that a powerful induction coil-machine, with the employment of very moderate battery-power, and of the new fuzes, would furnish with certainty, results of as great a magnitude as could be desired, and that its use would be less likely to be attended with difficulties than that of the hydro-electric or plate electric machine.

For all operations of a general character, however, the results

obtained up to the present time, have satisfactorily proved that the system of exploding charges, in the form of mines, for the simultaneous or regularly successive discharge of guns at a considerable distance, or for any similar purpose, by a magneto-electric current is, in point of certainty and simplicity, superior to any other which has hitherto received application.

XVI.—*On the Composition of a Carbonaceous Substance existing in Grey Cast Iron.*

By F. Crace Calvert, F.R.S., F.C.S.

Having often noticed that the quantity of carbonaceous mass left in the vessels in which grey cast iron was dissolved, varied with the concentration of the acid used, I began in September, 1858, a series of experiments on the action of very weak acids on cast iron, in the hope of obtaining a quantity of the so-called graphite which it contains, and I believe that I have arrived at results which throw much light upon the chemical composition of this substance, proving it to be composed of iron, carbon, nitrogen, and silicium. This substance occupies exactly the same volume as the cast iron from which it is obtained, and is sufficiently soft to be easily penetrated by a blade. I shall now describe the method of experimenting.

Cubes, of one centimetre in dimension, of Staffordshire cold-blast cast iron were placed in corked bottles with eighty times their volume of the following weak acid solutions:—

Sulphuric	acid,	1	alkalimeter	contained	10	grains of SO_3 anhydrous.
Nitric	,,	1	,,		13·5	,, NO_5 ,,
Hydrochloric		1	,,		9·12	,, HCl ,,
Acetic	,,	1	,,		12·75	,, $C_4H_3O_3$,,
Oxalic	,,	1	,,		9·00	,, C_2O_3 ,,
Tartaric	,,	1	,,		33·00	,, $C_8H_4O_{10}$,,
Gallic	,,	1	,,		10·00	,, cryst. acid.

The foregoing figures represent the equivalent quantity of anhydrous acid as compared with 10 grains of anhydrous sulphuric acid per alkalimeter.

Besides the above, phosphoric, carbonic, oleic acid, tannin, and acid peat-water were also used.

After three months of contact, I found that, although the external appearance of the cubes was not changed in any of the vessels, still those in contact with the weak sulphuric, hydrochloric, and acetic acid solutions, especially the latter, had become so soft externally that the blade could penetrate three or four millimetres into the cubes. I, therefore, removed the solutions from the vessels and replaced them by an equal bulk of each weak acid solution, and continued to do so every month for two years. I then found that the cubes in contact with the acetic acid ceased to yield iron to the acid, although they were still of the original size; they had, therefore, become transformed into the carbonaceous substance before mentioned. These are the results of the action of the various weak acid solutions, on the centimetre cubes of grey cast iron, after two years :—

Acetic acid . .	Complete.
Hydrochloric acid .	Nearly complete.
Sulphuric acid .	Ditto ditto.
Nitric acid . .	Action less complete than above.
Phosphoric acid .	No similar action.
Oxalic acid . .	Ditto.
Tartaric acid . .	Ditto.
Tannin . . .	Very slight action.
Carbonic acid .	Ditto.
Gallic acid . .	Ditto.
Oleic acid . .	Ditto.
Acid peat-water .	No similar action.

The action of acetic acid on grey cast iron is most interesting; for instead of ceasing when saturated with oxide of iron, as is the case with other acids, its action is continuous, if the precaution is taken to close the mouth of the vessel with an ordinary cork. Thus I have had cubes of cast iron in contact with the same quantity of acetic acid for two years, and the chemical action still existed when the contents of the bottles were examined. This action of acetic acid appears, therefore, to be analogous to that which it has on lead.

To examine the chemical composition of the cubes transformed by the action of acetic acid, they were reduced to fine powder in an agate mortar, and well washed with boiled water slightly acidulated with acetic acid. The powder was then dried at 115° C., in a dry atmosphere of carbonic acid or hydrogen, according to the nature of the body to be determined in the mass. The carbonaceous substance so prepared presented the following properties and composition :—

The cubes of grey cast iron, which originally weighed 15·324 grammes weighed only 3·489 at the end of the two years, and their specific gravity was reduced from 7·858 to 2·751. Their composition was as follows :—

	Composition of the original cubes.	Composition of the carbonaceous substance.
Iron . .	95·413	79·960
Carbon .	2·900	11·020
Nitrogen .	0·790	2·590
Silicium .	0·478	6·070
Phosphorus .	0·132	0·059
Sulphur .	0·179	0·096
Lost . .	0·108	0·205
	100·000	100·000

These results lead to the following remarks :—

Nitrogen.—That the largest part of the nitrogen originally existing in the cast iron remains in the graphitoid substance, and only a small portion is transformed into ammonia. These facts tend to prove that the nitrogen of cast iron exists in it under two states, namely, that one portion is combined with the carbon, whilst the other is in a condition to unite with the hydrogen liberated from the water, and thus to form ammonia. This method of ascertaining the amount of nitrogen in cast iron, by determining the quantity of nitrogen in the state of ammonia, and that existing in the carbonaceous mass, appears to be the best process known, for I obtained 0·790 from the same cast iron which only yielded me 0·100 by the process lately published by M. Fremy. For ordinary analyses of cast iron, the slow action of acetic acid may be advantageously replaced by that of hydrochloric acid, taking care to use freshly distilled acid, water free from ammonia, and placing the whole in a flask provided with cork

and tube, so as to exclude the possibility of the ammonia existing in the atmosphere from interfering with the experiment. By this means the amount of nitrogen existing in cast iron can be easily and speedily ascertained.

Silicium.—I have ascertained by direct experiments that it is silicium, and not silica, that enters into the composition of the carbonaceous mass. Amongst other experiments I may state that I took 5·96 grains of the carbonaceous substance dried at 115° C. in a current of carbonic acid, and after having placed it in a small platinum dish, the whole was introduced into a porcelain tube, and submitted for several hours at a red heat to a current of pure and dry oxygen. I then found that the 5·96 grains had increased to 7·39 grains, or nearly the theoretical amount: for 5·96 grains of substance would lose 0·664 of carbon, and the remaining 0·338 of silicium would become 0·718 of silica, whilst the 4·692 of iron would become 6·702 of peroxide of iron, or both added together 7·420, being within 0·13 grain of the weight actually found. Now, if the iron in the mass had been in the state of protoxide, and the silicium in the state of silica, the 5·96 grains employed would, after the loss of carbon, have decreased to 5·551 grains, leaving, therefore, no doubt that the carbonaceous substance contained metallic iron and silicium. Finding, however, that the quantity of silicium in the carbonaceous substance, though high, did not represent the whole of the silicium contained in the cast iron employed, I passed the hydrogen liberated by the action of weak acids on cast iron through fuming nitric acid, and found, on the evaporation of this acid, a white deposit of silica. All acids which give off hydrogen when in contact with cast iron, also give rise to the gas discovered by Wöhler, namely, silicide of hydrogen.

Carbon.—Like silicium, the quantity of carbon found in the carbonaceous compound does not represent the whole of the carbon pre-existing in the cast iron employed, as carburetted hydrogens are given off during the slow action of acetic acid on cast iron.*

Iron.—As shown by the above analysis, the carbonaceous compound contains 79·960 of metallic iron, even when the acetic acid has ceased to act upon it. I have made several experiments to satisfy my mind that the carbonaceous mass contains metallic iron, and not oxide of iron. Thus, I passed hydrogen, at a dull-red heat,

* I am now engaged in preparing a sufficient quantity of these hydrocarbons to enable me to submit them to a careful examination.

over some of the carbonaceous substance previously dried at 115°, and obtained no water, and the experiment related under the head of silicium confirms this conclusion. All grey cast irons appear to yield the same relative proportions of carbon and iron; but as cast iron becomes harder and whiter, the amount of carbon decreases, and, in fact, nearly disappears in Welsh white cinder iron, being replaced by silicium. The relative amount of carbon and iron in the carbonaceous substance corresponds to 4C and 6Fe, or are the same that I have found in some cast iron which had been saturated with carbon, by melting No. 1 cast iron in presence of a large excess of coke on a cupola, and called technically "keechy."

I do not, however, believe that the carbonaceous substance obtained by me is simply composed of 4C and 6Fe, but that the nitrogen and silicium found in it must likewise enter into its composition. But, in the present state of my researches, it would be premature to attempt to assign any definite composition to this substance. As I am, however, still pursuing the subject, I shall be happy, if I arrive at any conclusion, to communicate the same to the Society.

When the *graphitoid* substance prepared by the above process, is exposed to the atmosphere, it absorbs oxygen with rapidity, and the temperature of the mass rises rapidly, protoxide of iron being first formed, which is converted into sesqui-oxide; but when this mass is placed in distilled water, a chemical action ensues similar to that described by M. Kuhlmann, namely, a portion of the carbon is converted into carbonic acid by the oxygen of the sesqui-oxide of iron, and the carbonic acid thus produced unites with protoxide of iron to form carbonate of protoxide of iron. The atmospheric action on the carbonaceous substance above described explains the difference of composition which I have found to exist between the body obtained by me, and that of a soft graphitoid mass which was found to replace a mass of iron buried for many years amongst coal cinders, and which had the following composition:—

Mean of several Analyses.

Peroxide of iron	66·61
Carbon	12·03
Silica	18·13
Sulphur	0·79
Phosphorus	traces
Lime	2·14
	99·70

Nitrogen was also present, but its amount was not determined.

I am aware that the latter curious and interesting change in cast iron has been several times noticed. Thus, Dr. Henry published a short notice on this subject in the "Annals of Philosophy." Mr. R. Mallet also described a similar substance in the "Transactions of the British Association." Mr. Warington has also noticed the conversion of cast iron into a soft black substance which occurred in a brewery where it was in contact with sour beer. Lastly, Mr. E. W. Binney records, in the 11th volume of the "Memoirs of the Manchester Philosophical Society," a description of a similar substance found by him at the emptying of a deep coal-pit, in which the cast iron had remained submerged for a few years, and which yielded to Dr. Angus Smith the following composition:—

Iron and bases	38·8
Carbon	40·0
Silica	19·7
	98·5

In conclusion, the conversion of the guns of the "Royal George," at Spithead, is so well known, that I merely refer to it to express the same opinion as Mr. Binney,—that it strongly behoves those who have charge of lighthouses, now so often erected in the sea upon cast-iron pillars, to carefully and frequently inspect such structures, for day by day their support must be weakened by the action of the salt-water. (See Memoirs of "Manchester Philosophical Society, Vol. II., page 28.)

XVII.—*On the Bromide of Carbon.*

By Arthur E. W. Lennox.

The compounds of carbon with bromine have as yet received but limited attention. The tetrabromide of carbon—CBr_4 of the methyl series—is altogether unknown. Kolbe failed in obtaining this compound by submitting disulphide of carbon, at a high temperature, to the action of bromine; and I learn from Dr. Hofmann, that the action of pentabromide of antimony on the disulphide gives no better result. The bromide of carbon C_2Br_4, has been obtained by Lœwig*, who procured this substance by the action of bromine on alcohol or on ether, when it is formed according to the equations—

$$C_2H_6O + 4\,Br_2 = C_2Br_4 + 4HBr + H_2O.$$
$$C_4H_{10}O + 8Br_2 = 2C_2Br_4 + 8HBr + H_2O.$$

These processes appear, however, to be attended with difficulties. At all events, Vœlckel†, who repeated Lœwig's experiments, failed in obtaining the substance described by that chemist.

A simpler method for obtaining this bromide of carbon appeared to present itself in the perfect substitution of bromine for the hydrogen of olefiant gas.

The brominated derivatives of ethylene have been chiefly examined by Regnault and by Cahours, and, more recently, by Wurtz and by Sawitch. The following terms have been obtained:—

Dibromide of ethylene	$C_2H_4Br_2$.
Dibromide of monobrominated ethylene .	$C_2(H_3Br)Br_2$.
Dibromide of dibrominated ethylene .	$C_2(H_2Br_2)Br_2$.
Dibromide of tribrominated ethylene .	$C_2(HBr_3)Br_2$.
Monobrominated ethylene . . .	C_2H_3Br.
Dibromated ethylene	$C_2H_2Br_2$.

* Ann. Ch. Pharm., iii, 292.

† Ibid., xli, 119.

It thus appears that the whole series has been obtained, with the exception of the tetrabrominated ethylene, which would be the bromide of carbon obtained by Lœwig in the reaction above indicated.

Of the brominated derivatives of ethylene, dibromide of ethylene, monobrominated ethylene (bromide of vinyl), and dibromide of monobrominated ethylene, have as yet been best investigated. In re-examining these substances, in transforming dibromide of ethylene, by the action of an alcoholic solution of potash, into monobrominated ethylene, and the latter, by treatment with bromine, into the corresponding dibromide, I had an opportunity of tracing, step by step, the observations of my predecessors.

The action of an alcoholic solution of potash upon the dibromide of monobrominated ethylene yields, together with secondary products, a comparatively small quantity of the oily compound $C_2H_2Br_2$, which is still further diminished by the extraordinary property exhibited by this substance of undergoing a molecular transformation similar to that of dichlorinated ethylene, as observed by Regnault,* and of monobrominated ethylene, more recently examined by Dr. Hofmann.† Dibrominated ethylene having been lately the subject of a more minute investigation by M. Sawitch,‡ I have not entered upon a more close examination of this body, but have at once, by the renewed action of bromine, converted it into the

Dibromide of Dibrominated Ethylene.

Bromine attacks the dibrominated ethylene with the greatest energy, heat is evolved, and the bromine disappears. When the bromine was no longer fixed, the orange-yellow liquid was treated with a weak solution of potash, washed with water, and ultimately distilled with precaution. It boils at about 200° C., but not without partial decomposition, white fumes containing hydrobromic acid being given off during ebullition, which powerfully and persistently attacked the eyes.

The bromine-compound is insoluble in water, but dissolves readily in alcohol and in ether; when exposed to a freezing mixture it solidifies to a white crystalline mass. As it was found impossible to purify this substance for analysis by distillation, a current of

* Ann. Ch. Phys. [2.] lxix, 151.

† Chem. Soc. Qu. J., xiii, 68.

‡ Bulletin de la Société Chimique de Paris, 1861, p. 7.

perfectly dry carbonic acid gas was passed through the liquid heated in a water-bath to about 75° C. After a time it assumed a lighter colour, and no longer gave off hydrobromic acid.

047·0 grm. of substance burnt with lime gave 1·016 grm. of bromide of silver.

The formula.

$$C_2 H_2 Br_4$$

requires the following values.*

	Theory.		Experiment.
C_2	24	„	„
H_2	2	„	„
Br_4	320	92·40	91·97
	346		

Tribrominated Ethylene.

The dibromide previously described is powerfully acted upon by an alcoholic solution of potash:

$$C_2H_2Br_4 + KHO = C_2HBr_3 + KBr + H_2O.$$

Addition of water to the alcoholic solution precipitates the tribrominated ethylene as an oily substance, boiling at 130° C, which, by digestion over chloride of calcium and subsequent careful distillation, may be obtained sufficiently pure for analysis.

0·342 grm. of substance burnt with lime, furnished 0·726 of bromide of silver.

The formula,

C_2HBr_3 requires,

	Theory.		Experiment.
C_2	24	„	„
H	1	„	„
Br_3	240	90·56	90·32
	265		

Tribrominated ethylene, like the other substitution-product of ethylene, is apt to furnish an isomeric solid, which is readily soluble in alcohol and in ether, from which it crystallises in colourless plates. On slowly evaporating a solution of the oily modification in alcohol or ether, the crystalline solid is likewise obtained.

* H = 1; O = 16; C = 12; Br = 80.

Dibromide of Tribrominated Ethylene.

To obtain this compound, tribrominated ethylene was introduced into a retort, and cautiously distilled into a receiver containing bromine. Combination took place with considerable evolution of heat. The orange-yellow liquid thus produced was washed with weak potash, and ultimately with water. Thus purified, this bromine-compound is a yellowish red oil, soluble in alcohol and ether, and solidifying when exposed to a frigorific mixture. I have not succeeded in preparing this substance in a state of sufficient purity for analysis; but its nature is sufficiently established by the facility with which it is transformed into tetrabrominated ethylene, or bromide of carbon, by the action of alcoholic solution of potash.

Addition of water to the alcoholic solution precipitates this compound as an oily liquid, which, when slowly deposited by spontaneous evaporation from its solution in alcohol or ether, separates in beautiful crystalline plates of an agreeable aromatic odour and burning taste: one or two crystallisations render it perfectly pure. It is heavier than water; fuses at 50° C; sublimes at a higher temperature; and is not attacked by the mineral acids. These properties identify this compound with the bromide of carbon which Lœwig obtained by the action of bromine upon alcohol and upon ether. For analysis it was dried over sulphuric acid in vacuo, and has furnished the following results

0·315 grm. of substance burnt with a mixture of oxide of copper and chromate of lead gave 0·078 carbonic acid.

0·175 grm. of substance burnt with lime gave 0·330 grm. of bromide of silver.

The formula,

$$C_2Br_4$$

requires the following values.

	Theory.			Experiment.
C_2	24	..	6·98	6·69.
Br_4	320	..	93·02	92·57.
	344			

The tetrabrominated ethylene is generated by the action of

an alcoholic solution of potash upon the dibromide of tribrominated ethylene, according to the following equation:

$$C_2HBr_5 + KHO = C_2Br_4 + KBr + H_2O.$$

The experiments which form the subject of this note were performed in the laboratory of Dr. Hofmann.

XVIII.—*On the Power ascribed to the Roots of Plants of rejecting Poisonous or Abnormal Substances presented to them.*

By Charles Daubeny, M.D., F.R.S., M.R I.A., Foreign Associate of the Royal Academy of Munich, &c., and Professor of Botany, Oxford.

Before reporting to the Society the results of a few experiments which I have lately made on the subject of the absorption of mineral bodies by the roots of plants, it may not be amiss for me to enter into some general account of the state of our knowledge relative to the subject referred to, including a brief notice of the experiments tending to elucidate it, which have been already communicated to the public by myself and others.

I may in the first place remind you, that, with regard to the functions of the roots, two opposite views have been entertained: the one, that they consist simply of a system of cells, surrounded by membrane, which possesses no peculiar properties, but is capable, by virtue of endosmose, of absorbing any fluid that happens to lie in contact with their external surfaces, and, by the force of capillarity, of transmitting the same afterwards to the parts above: the other, that as vital organs, they are endowed with a certain power, which seems to us analogous to selection, or, at least, answers the same purpose; in consequence of which they abstract from the fluid presented to them those principles which are required for the general uses of their own economy and that of the plant in general.

The former, doubtless, is the more readily intelligible hypothesis, and is one in support of which many facts may be alleged.

Saussure, for instance, found, that when the roots of a water-plant, such as the *Polygonum Persicaria,* were immersed in water containing equal quantities of various saline and other soluble bodies, the latter were absorbed, not in the ratio of their respective fitness for supplying the wants of the system, but in proportion to the facility with which the solution was capable of entering the spongioles, and of flowing through the tissues of the plant.

Gum and humus, for instance, being viscid, entered the spongioles in much smaller quantity* than various saline bodies did, which might be regarded as less needed by the plant which absorbed them.

But, of all those tried, no one was taken up in such large quantities as sulphate of copper; a circumstance which may be attributed to the poisonous and corrosive quality of this substance, owing to which the texture of the cells became disorganized, and the entrance of the solution into the vegetable texture took place as freely, perhaps, as if the parts had been actually severed asunder.

These statements of Saussure were confirmed by Sir Humphry Davy, who, in his "Agricultural Chemistry," pointed out, that saline solutions are absorbed more readily when in a diluted state than when concentrated.

Later experimentalists have even gone so far as to contend, that, with the exception of such salts as those of copper, which destroy the texture of the roots, all solutions are absorbed with equal readiness. Such was the conclusion arrived at by Dr. Lindley, from researches of his own, which are detailed in vol. XVIII of the "Annals of Natural History."

The experiments of Boucherie have also been appealed to, as affording an argument from analogy in support of this same view. In these, openings were made in the lower part of the trunks of various trees by sawing out a portion of the wood, and a water-proof bag was placed round the severed portion, so that a saline solution might be introduced, which was rapidly absorbed by the tree, of whatever nature it might be.† Through this device, wood became impregnated with various metallic salts, by which its hardness and durability are augmented in a remarkable degree.

Similar experiments have been instituted by Mr. Hyett, of

* The late researches of the Master of the Mint on endosmose may serve to explain this, on the principle that gelatinous bodies do not pass through membrane.

† Annales de Chemie, vol. lxxiv, p. 113.

Painswick House, near Gloucester, the results of which are given in vol. VIII of the "Transactions of the Highland Society," published in 1843.

The same inference has been deduced from observations made as to the influence exerted upon the constitution of a plant by the quality of the soil, or by the nature of the ingredients present in it which are submitted to its roots.

This influence was shown by the experiments of Saussure, where a fir, which had grown at Mont Breven on a dolomitic rock, was proved, when burnt, to contain, in its ashes, a certain percentage of magnesia; whilst the same species from Mont la Salle, a granitic rock, was destitute of magnesia, but possessed an equivalent increase in the lime and potassa belonging to it; and likewise from those of Berthier, showing, that the ashes of a fir which had grown in Norway, yielded only 16·8 per cent. of alkalies, 29·6 of lime, and 3·3 of magnesia, whereas the same kind of timber from Allevard, in France, afforded 34·7 of alkali, 13·6 of lime, and 4·35 of magnesia.

Such are the principal facts that may be appealed to in support of the hypothesis, that roots are merely passive instruments, which take up whatever is presented to them without selection or preference.

It must, however, on the other hand, be observed, that the properties of endosmose, capillarity, and the like, to which the absorption of saline fluids by the roots, and their transmission through the stem, may be attributed, are common to all tissues similarly constituted, whether dead or living; and that the co-existence of other properties more especially vital, is by no means excluded by their presence.

It is just the same, indeed, with the animal kingdom. No one doubts, that the living organism of animals is amenable to the common laws of matter, however much the latter may be controlled, and masked, as it were, by the forces of life.

That in the case of the spongioles also, similar functions dependent upon vitality must be assumed to be superadded to those common to matter generally, may be argued from the fact, that the power of substituting one ingredient for another is at any rate circumscribed within very narrow limits.

The most trustworthy experiments hitherto made appear to show: 1st. That it is impossible to replace any of the bases or

acids which usually enter into the composition of the vegetable by any other of the same series which are not usually present: 2ndly, That even those bases which are capable, to a certain extent, of replacing each other, cannot do so indefinitely: and, 3rdly, That much of the difference in composition which has been remarked as existing between plants of the same species, growing in different soils, or manured in various ways, may be accounted for by the predominance of one or other of its proximate principles in the several samples submitted to examination.

Thus wheat cultivated in one soil, may contain more gluten and less starch than in another, and hence the chemical constitution of the grain must in each instance necessarily vary.

In support of these positions, I will appeal to some experiments of my own already published, as well as to those of others; and I will also allude to certain facts of general notoriety which seem to me to point in the same direction.

In the Transactions of the Linnæan Society, vol. xvii, published in 1835, I showed, that plants watered with a solution of nitrate of strontia, and seeds sown in soils containing the sulphate of the same earth, never appeared to absorb any portion of this base: for it could not be detected in their stems, leaves, or flowers, and only in the minutest quantity in, or attached to, their roots.

In relating these experiments, I took the opportunity of alluding to an analogous result obtained by myself with reference to the animal kingdom, where hens, allowed access, during the breeding season, to sulphate of strontia, but to no other earth, laid eggs with soft shells.

I may also appeal to the notorious fact, that no acid can replace the phosphoric in the vegetable organism; a principle upon which the entire theory of scientific agriculture, as expounded by Liebig and others, seems to be based. Were this not the case, the necessity of supplying, from time to time, the mineral phosphates, as fast as they are drawn off by successive crops, might be superseded by other expedients. Some interesting experiments, bearing upon this subject, are reported on the authority of the Prince of Salm Horstmar, in the Annales de Chimie, for 1850, vol. xxxiii. The Prince moulded some little wax vessels, in height about $2\frac{1}{4}$ inches, and in diameter 1 inch, and filled each of them either with pure sand, or with powdered rock-crystal which had been previously calcined. Into these vessels were introduced a

few grains of oats, and along with them a minute quantity of one or more of the ingredients which, by analysis, this plant has been found to contain.

The following were the results arrived at:—

1. When neither any inorganic nor nitrogenised materials had been added, the oats sprouted, but came up weak, and were reduced to two flowers and a single fruit.

2. When nitrogenised substances were added, the plant shot up higher, but was too feeble to sustain itself in an erect position.

3. When denied access to nitrogenised materials, but supplied with all the inorganic principles normally present in it, namely, with silica, potassa, lime, magnesia, and oxide of iron, together with phosphoric and sulphuric acids, the plant was small and languid, and whilst the formation of flowers took place to a more limited extent than in the former case, that of grain was altogether wanting.

4. When both the mineral substances above enumerated and the nitrogenised matters were present, there was an increase both in the vigour of the plant and in the number of its flowers; but still something appeared to be wanting in the pulverized quartz, which existed in the river sand; for, although lateral shoots were produced, showing a power of development to reside in the plant, still the regular formation of grain did not take place.

5. But when any one of the above seven inorganic substances was wanting, its development became in some way or other arrested.

Thus when magnesia was not supplied, the growth of the plant was feeble; when potassa, it was stunted, and only a single stem produced; when soluble silica, the growth of the stem was arrested; when phosphoric acid, only one flower was obtained, and this did not produce grain; when sulphuric acid was not supplied, there was no stem, and the plant died before the third leaf had been produced; and when iron was wanting, the plant was deficient in its natural green colour.

The experimental results above obtained are decidedly adverse to the idea, that even normal substances can replace each other indefinitely in the structure of a plant, showing, as they seem to do, that the constituents are all of them indispensable to their healthy growth.

The fourth conclusion indeed arrived at, namely, as to the imperfect development of a plant grown in powdered quartz, even where all the bodies known to be essential to it are provided; although it arrives at a perfect state of maturity, in all respects,

when grown in river sand, seems to indicate, that we are still unacquainted with all the ingredients of the soil and of the plants grown in it.

This is the point, therefore, towards which our inquiries should be directed, and which the Prince himself, at the end of his Memoir, proposes to investigate. As, however, ten years have since elapsed without any further communication from him having reached my knowledge, I conclude that we must not expect any further elucidation of the subject from this quarter.*

In the interval, however, the remarkable researches of Bunsen and Kirchhoff, on Spectrum Analysis, have established the existence in nature of some substances hitherto unsuspected, and the wide diffusion of others hitherto regarded as of great rarity; so that, as I perceive has been already suggested by Dr. Cameron in a paper read before the Dublin Society,† the failure of our crops may, in certain cases, be owing to the absence from the soil of some ingredient hitherto overlooked, such for instance as lithium, or the new alkali-metal cæsium, which had been withdrawn by preceding crops, and not restored by the species of manure which had been subsequently applied.

If then, it be true, that abnormal substances cannot supply the place of normal ones, and, therefore, do not enter into the organisation of a plant, we have only the alternative of supposing, that when brought into contact with the roots, the former either are not admitted at all into the system, or are afterwards excreted from it.

Of the two, the former would seem to be the more legitimate inference; for if these bodies had been excreted, we ought to find traces of them *in transitu* distributed throughout the various tissues of the plant.

The latter is, indeed, actually found to be the case, when substances of this nature are brought into contact with the cut surfaces of the stem or roots, as in the experiments of Boucherie; or even when the vitality of the root is destroyed by the applica-

* Since the reading of this Paper, I have found, from a late notice in the Chemical News, copied from Poggendorff's Annalen, that the Prince now believes lithia to be indispensable to the development of grain, he having lately found, that barley did not come to maturity in coarsely powdered and washed rock-crystal, even when supplied with carbonate of lime, magnesia, and manganese, sulphates, phosphates, and fluoride of potassium; but that the addition of nitrate of lithia in the proportion of the 100th of a milligramme, caused it to flower, and to yield perfectly ripe grain.

† See the Gardeners' Chronicle for March 29, 1861.

tion to it of a poisonous or corrosive substance, as in the cases reported by Saussure.

On this principle, indeed, it is easy to colour the stem of a plant blue, by first immersing its roots in a solution of sulphate of iron, and afterwards in one of ferrocyanide of potassium, when the ferrocyanide of iron will be found wherever the solutions intermix. But no such transmission upwards would seem to take place when an abnormal substance is brought into juxta-position with a living root, until its organisation is destroyed either by mechanical means, or by the poisonous influence of the application itself.

The case, however, is different, when we employ substances normally present in the plant. Here there can be no doubt, that the substances do obtain admission into the system, and that the usual proportions of the respective ingredients may be made to vary, by supplying the roots more plentifully with one ingredient than with the rest.

It has been stated, for instance, by Will and Fresenius, that wheat cultivated near the sea contains more soda and less potassa than it does in more inland situations; and although certain analyses made in my laboratory by Mr. Way, some years ago, would lead to the contrary conclusion, yet in a Memoir read before the Chemical Society in 1853, I brought forward facts which lend support to the view taken by the German chemists, by showing that the relative proportions of potassa and soda present in barley varied, according as the soil was more or less impregnated with one or other of these alkalies.

It will be seen, by reference to the report of these experiments contained in the Chemical Journal, that in this manner the proportion of soda to potassa was made to vary from 23·5 to 15·5 in the grain, and from 27·25 to 20·0 in the straw, thus appearing to show that, to a certain extent, one alkali might replace the other in the vegetable organisation.

But the latest and most extensive series of investigations bearing upon this subject are those by Malaguti and Durocher, recorded in the Annales de Chimie for December, 1858.

The primary object of these chemists was to determine, whether any relation subsisted between the mineral constitution of a plant and its organic structure, as evidenced by the place it occupied as a member of one of the natural families into which the vegetable kingdom is divided.

For this purpose they examined the ashes of 150 plants, selected

from twenty-five different natural families, and growing spontaneously in the soil of France, analysing at least three species of each family, in order to estimate the range of variation occurring in them, and distinguishing the arborescent from the herbaceous, as containing a different amount of ligneous fibre.

In the course of these inquiries, two facts were elicited, both of which accord with the results obtained by myself from the experiments above referred to; the first, that plants must possess a power of selection, inasmuch as several species growing on the same soil, abstract from it different amounts of the normal constituents presented to them (see p. 289); the second, that the same species, raised upon different soils, vary to a certain extent in their mineral constitution.

Thus, in argillaceous soils, the proportion of chlorine in the plant is, in general, less than it is in calcareous ones, the range of variation being from 4 to 20 per cent. On the other hand, the amount of sulphuric acid will be greater in argillaceous than in calcareous soils; and the same remark applies, although in a less degree, to the phosphoric acid also.

In like manner, plants grown on calcareous soils contain, in general, more soda and less potassa than in argillaceous ones. Thus, in *Brassica napus* there was present, of soda 5·50, and of potassa 12·34, when grown on a limestone; and of soda 3·00, potassa 25·00 when cultivated upon clay.

Similar differences are pointed out as existing in the case of *Trifolium pratense* and *T. incarnatum*, &c., showing the dependence of the alkaline ingredients upon the chemical constitution of the soil in which these plants were reared.

Liebig, in his Agricultural Chemistry, has pointed out, that in these cases of substitution, the absolute amount of bases present must be exactly equivalent to the acids which the plant contains, or, in other words, that the sum of the oxygen in them is invariable.

Thus, according to Saussure's analysis already referred to, 100 parts of the ashes of a fir from Mount Breven contained—

Carbonate of potassa	.	3·60	in which the O was	0·415
„ Lime	.	46·34	„	7·327
„ Magnesia		6·77	„	1·215
			Total of O .	9·007

whilst trees of the same species from Mt. la Salle contained:—

Carbonate of	Potassa . .	7·36 in which the O was	0·850
„	Lime . . .	61·19 „	8·100
„	Magnesia .	0·00	
		Total of O	8·950
		Difference only . .	0·057
			9·007

And in like manner the ashes of a fir from Allevard, according to Berthier, contained

Of potassa and soda together .	16·6	containing of O=	3·57
Lime	29·6	„ „	8·36
Magnesia	3·3	„ „	1·26
			13·10

whilst those of one from Norway contained

Of potassa . .	14·10	containing of O =	2·40
Soda . . .	20·70	„ .	5·30
Lime . . .	13·60	„ .	3·82
Magnesia .	4·35	„ .	1·69
			13·21
		Difference .	11
			13·10

These remarkable approximations equally attest the accuracy of the analysts, and the acuteness of the reasoner who first pointed out the relations between the two;—they prove, that the amount of bases is determined by the quantity of acids contained in certain tissues of the plant, and that this amount, however much the nature of the acid may vary, is in each case definite.

But although the quantity of bases present is necessarily dependent upon the amount of acid contained within the plant, it does not follow that even isomorphous bodies, such as potassa and soda, and still less other bases, as lime and magnesia, are capable of replacing each other throughout the entire organism.

The contrary, indeed, would seem, from the following considerations, to be the more probable hypothesis.

In the experiments performed by myself, which have been

already noticed, it may be remarked, that the difference in the relative proportions of soda and potassa never rose above 8 per cent.; and yet, if this proportion of soda had taken the place of potassa as a constituent in the organism of a plant, one does not see why the same might not be the case with respect to the whole. On this supposition, the organs of plants would, like the different varieties of augite, garnet, &c., have no definite or fixed composition, the only condition being that their elements should be isomorphous: a position well established with regard to the mineral kingdom, but scarcely applicable, one would think, to the vegetable.

Perhaps the strongest proof that can be adduced in favour of the necessity of a certain fixed chemical constitution for the existence of plants is supplied by the case of those which derive their nourishment from sea water.

If we examine chemically any of the marine algæ, we shall find, that, although containing a considerable proportion of soda, yet, that in many of them, there is present an almost equal amount of potassa. Thus, in the 4th edition of Liebig's Chemistry of Agriculture, 1847, is given the analysis of four species of *fucus*, two of *laminaria*, and twelve of other kinds of algæ. Four of these analyses were made in the laboratory of Giessen; and for the remainder we have the authority of Forchhammer; they present, indeed, many discrepancies, but, upon the whole, concur in establishing, that potassa as often exceeds soda in the constitution of an alga, as the reverse.

I should, indeed, from the difference in the results obtained, be tempted to infer, that a large but variable quantity of sea-water had been circulating through the tissues of the sea-weeds at the times when they were severally collected, and that this had been included in the respective analyses. At any rate, if soda were capable of replacing potassa in the system of a plant, one does not see, why any potassa at all, except an infinitesimal quantity, should be present in them, considering that sea water, which alone can supply the mineral constituents present in the organisation of a marine plant, contains an infinitely smaller amount of potassa than it does of soda.

The case might have been put even more strongly, if I had adverted to the quantity of iodine which sea plants extract from the waters of the ocean, although the proportion of that ingredient, which is known to exist in the latter, can, from its minuteness, be hardly detected, even by the most delicate tests.

Hence iodine, as it would seem, can no more be replaced by chlorine in the organism of marine plants, than potassa can by soda, although both the one and the other are regarded as isomorphous.

Liebig, in his Letters on Modern Agriculture (page 44), has illustrated this principle by the case of the common duckweed of our ponds, the *Lemna trisulca*, growing in a bog, the water of which contained the following salts, in such proportions, compared with those present in the plant, as indicated a power of selection residing in the latter.

Thus there were present in seventy-six parts:—

	of the soil	of the duckweed.
Lime	35·000	16·820
Magnesia	12·264	5·080
Chloride of sodium	10·100	5·897
Potassa	3·970	13·160
Soda	0·471	..
Oxide of iron and traces of alumina	0·721	7·360
Phosphoric acid	2·619	8·730
Sulphuric acid	8·271	6·090
Silica	3·240	12·250
Chloride of potassium	..	1·450
Total	76·656	76·837

We must here admit a certain power of selection residing in the roots of the plant, since, whilst the water contained in 76 parts, of lime about 35, and of magnesia 12 per cent., the plant had abstracted only 16·8 of the former, and 5 of the latter element; and whereas the proportion of potassa in the water was less than 4, that in the plant was 13; of phosphoric acid in the water 2·6, in the plant 8·7; of silica in the water 3·2, in the plant 12·2.

But, in fact, we need not go so far for proofs of this familiar principle; for, as every plant possesses a different chemical constitution, it is evident that of several species grown in the same soil, each one must exercise a kind of selection, in order to extract from the same material the several ingredients which it requires for its separate organisation.

I have already* attempted to reconcile the apparent discrepancy

* See vol. v. of this Journal, 1853.

between the above two classes of phenomena,—namely, the variations in the composition of a plant which may be induced by artificial means, and the necessity for the presence of certain specific mineral ingredients in their organisation, by supposing that the proximate principles existing in a vegetable are fixed and invariable, a seed possessing a certain percentage of phosphoric acid which cannot be replaced by any other ingredient, a mass of ligneous fibre a certain amount of potassa, &c.; but that, independently of the acids and bases which enter into their composition, and make up the fabric of the plant, there is always circulating through its tissues a certain amount of alkali, one function of which, according to Liebig, is to promote the fixation of carbonic acid; and that, as the latter duty may be discharged by one alkali as well as by another, it is conceivable, that potassa and soda, or even lime and magnesia, may replace one another, so far as respects the fluids which are circulating through the vegetable tissues.

Hence we may understand, how it is, that one portion of the alkaline or other mineral ingredients, present in a plant, may be definite as to quality, whilst another portion may vary according to circumstances; and accordingly, whilst it is found that each proximate principle presents a fixed chemical composition, the entire plant may, nevertheless, vary within certain limits, as it will contain an uncertain amount of unassimilated sap flowing through its system at the time when it was cut down.

There is also another cause for the different composition of the ashes of the same species of plant, namely, a variation in the ratio subsisting between the proximate principles themselves. Thus, one particular climate, or mode of culture, may favour the production of gluten, another that of starch; and thus the seed of the same plant, in different localities, may not always be identical in point of composition. Thus, I have given instances, in my "Lectures on Agriculture," published in 1841, in which the application of nitrate of soda to a soil added 4·25 to the amount of gluten present in the crop of wheat growing in it; and Davy affirms that the flour of warm climates contains, in general, more gluten than that of colder ones.*

Upon the whole, then, I should be inclined to infer, that the spongioles of the roots have residing in them some specific power of excluding those constituents of the soil which are abnormal, and,

* See also Boussingault, Ann. Ch. Phys. [2], lxv, 301.

therefore, unsuitable to the plant, but that they take up those which are normal in any proportions in which they may chance to present themselves; the redundant portion, however, left after the necessities of the organism have been provided for, being again excreted, so that a vegetable will only vary in mineral composition in proportion to the relative amount of the several proximate principles which may be produced under the peculiar circumstances of its cultivation, or of the climate it enjoys.

If it be questioned, whether we can concede to the absorbing surfaces of the roots a function so nearly allied, in semblance at least, to volition, I would refer to the observations of Huxtable and Thomson, and more especially to the valuable Memoirs of Way, as establishing the existence of a property connected with these organs of no less extraordinary a nature; namely, that whilst the carbonate of ammonia, present in rain-water and in manures, is so firmly fixed in the soil, that, under ordinary circumstances, water containing carbonic acid seems unable to withdraw it, the same is nevertheless commonly absorbed and conveyed into the tissue of plants by means of their roots.

Hence, as Liebig observes, vegetables must obtain their nourishment by virtue of some specific attraction exerted by the rootlets upon the ingredients locked up within the earth; a property, wonderful, indeed, but not more so, than that possessed by the leaves, of converting carbonic acid into other organic principles by the elimination of oxygen.

In a Paper published in the Philosophical Transactions for 1836, "On the Action of Light upon Plants, and of Plants upon the Atmosphere," I concluded, that light operates upon the vegetable, as it does upon the animal kingdom, in the character of a specific stimulus, so that the formation of the various secretions elaborated from the carbonic acid absorbed, is not a purely chemical process, but is due to some peculiar agency of the green parts connected with, and dependent upon, their vitality.

I would now extend the same inference to the roots, considering that, when in a healthy and vigorous condition, they serve as instruments for conveying to the other parts of a plant those juices, which contain substances calculated for affording them nourishment, and for excluding others which might be useless or injurious to them.

Liebig, indeed, goes so far as to contend, that the mineral matters presented to the spongioles are not in a soluble form; for

if they were, he suggests, that water, either alone or in conjunction with carbonic acid, would be capable of abstracting them from the earth. He therefore imagines, that, being distributed over the general body of the soil in a finely divided condition, they are taken up by the rootlets, owing to a kind of specific attraction. We can thus more readily understand, how it is that certain ingredients are absorbed in larger quantities than others, and why some even should be absolutely rejected, as in the case of the common duckweed, to which Liebig refers.

It is remarkable that, although alumina is not usually present in the ashes of plants, yet that one tribe, namely, the *Lycopodiaceæ*, contains it in large quantities,*—a fact which I have myself verified.

By what precise agency this usually insoluble earth† finds its way into the vegetable economy seems to be yet undetermined; but its occurrence in a few plants may be regarded as a proof that it would have been taken up in all, if the spongioles were merely passive instruments for absorbing and transmitting indiscriminately whatever was presented to their external surfaces.

But, indeed, the whole efficacy of geothermal culture, now so much insisted on by horticulturists, seems to pre-suppose, that the roots are vital agents, capable of being acted upon by stimuli. Why else should the application of heat to the roots impart greater vigour to the upper parts of a tree, and cause, as in the case of the *Bougainvillea*, the copious development of flowers where none before were produced; and, on the other hand, why, as happened in so many cases during the late severe winter, should the plant be destroyed in consequence of the cold penetrating into the ground, whilst it resisted the influence of the frost so long as its roots were protected?

If the spongioles acted upon the surrounding matter simply by virtue of endosmose, as a dead membrane might do, the process of absorption, although it might be arrested by frost, would be renewed when the mild weather returned, and the plant would sustain no further damage than what might be due to a temporary suspension of its functions; whereas the consequence of the late

* *L. chamæcyparissus*, 39·07; *L. clavatum*, 20·69; according to Ratthausen, in Liebig's "Jahresbericht" for 1853, p. 586.

† The late researches of the Master of the Mint, which were not known to me at the time of the reading of this Paper, show that alumina is capable of existing in a soluble condition combined with water.

extreme cold appears to have been, that the roots became unfitted for discharging their office, and that the stem and branches suffered, not only negatively, by the deprivation of proper nourishment, but positively, by receiving noxious matter from the ground. In short, the spongioles may be supposed to have been reduced to the same condition by the cold, as that to which they would be brought by the application of a poisonous solution, such as the sulphate of copper already alluded to; and in both cases the same consequences would ensue.

Let us now consider, how the influence of poisons upon the vegetable economy is to be reconciled with the principles just laid down.

It is notorious, that a moderate dose of certain mineral as well as of vegetable poisons applied to the roots of a growing plant destroys its vitality, as certainly and as speedily, as if the same were injected into any part of the stem or branches. It is, therefore, evident, that the poison does not merely exert a *local* influence upon the part to which it is applied, but that it must be absorbed and transmitted through the other parts of the organism. But how, it may be asked, is this fact to be reconciled with the power of rejecting such abnormal ingredients as are presented, which we have ascribed to the roots?* The reason I conceive to be, that the deleterious quality of the substance destroys the vitality of the part, and thus reduces it to the condition of a simple membrane, which by endosmose absorbs whatever is presented to its external surfaces.

The same thing may be supposed to happen generally in the case of poisons of a certain degree of intensity, as in that of the solution of sulphate of copper, which Saussure and others have fully ascertained to be taken up in larger quantity than any other soluble material. In all such instances, however, the absorption of the poison was speedily followed by the death of the plant.

When, on the contrary, the poison is presented in a more diluted form, the effect resulting would seem to be a matter of rather greater uncertainty, as the statements made on the subject

* One of the few cases recorded, on competent authority, in which an abnormal substance appears to be taken up by a plant, without, apparently, affecting its healthy condition, is that of the violet which grows on the calamine rocks near Aix la Chapelle, and is found to contain zinc amongst its mineral constituents.—See Annals of Natural History, vol. xiv, second series, for 1854.

are of a conflicting nature. On the one hand, Dr. Edmund Davy, Professor of Agriculture and Agricultural Chemistry in the Dublin Society, is quoted in the Gardener's Chronicle for September 10th, 1859, as having ascertained, that peas watered with a saturated solution of arsenious acid for more than a week continued to the last uninjured, although arsenic was readily detected by appropriate tests in the plants subjected to this treatment. He is also reported to have stated, that a solution of superphosphate of lime, which, if impure sulphuric acid has been employed in its preparation, always contains more or less arsenic, was applied to a cabbage plant, which nevertheless grew and flourished, although arsenic was detected in it afterwards. A similar experiment was tried also upon turnips with the same results. Mr. Horsley, of Cheltenham, has since published a letter addressed to Dr. Edmund Davy, in which he confidently affirms the same fact, and assures us that it holds good in the case of all the various plants upon which he had experimented.

On the other hand, Jäger, Humboldt, and Link could not induce plants to grow when sprinkled with arsenicated water, and Mr. Ogsden (in the Gardener's Chronicle for March 10th, 1860,) states, that on repeating Davy's experiments, he found cabbage plants, and also Scotch kale, to droop and die within a week after the application of the arsenical solution. In neither of these cases was any arsenic detected in the leaves, or higher up in the stem, than about 5 inches from the ground.

In corroboration of these results, it might be unfair to add those arrived at by Marcet, as he plunged the shoot of a kidney-bean, and not its roots, into the arsenical solution made use of, which contained, it seems, 2 grains of arsenious acid in 2 ounces of water. Under such circumstances, the death of the plant which ensued cannot well be cited as an argument from analogy as to what might happen in the case of the spongioles of the roots; but the immunity which the potatoe crop in the neighbourhood of Swansea seems to enjoy from the influence of the arsenical fumes with which the atmosphere thereabouts is so infected, and likewise the fact, that, in certain parts of Cornwall, where arsenical pyrites from the mines is thrown upon the soil in large quantities, the crops do not appear to suffer, and contract, in consequence, no injurious properties, may perhaps be fairly adduced in support of this same conclusion.

I will now lay before the Society a few experiments bearing upon the same subject which have been carried on by myself.

I possess, in the first place, some notes of an experiment made so long ago as 1837, in which plants were watered with a solution of arsenious acid in the proportion of 1 grain of the mineral to 3 pints of water, and where no trace of arsenic could be detected in them after the application.

Passing over these trials, which appear wanting in the requisite precision, I will state what I have done during the past year, with a view of determining the power of the roots to absorb poisons and abnormal substances, when presented to them in a state of great dilution.

Having first made a few tentative experiments on a small scale, with the view of ascertaining what amount of arsenious acid might be applied to a growing plant with impunity, I watered a plot of ground, 25 feet long by 4 feet wide, containing a crop of young barley, with a solution of arsenious acid, in the proportion of 2 ounces to 10 gallons of water. Finding, six days afterwards, that the barley appeared to be blighted, I applied to a second plot, of the same dimensions, a solution of just half the strength of the preceding, containing 1 ounce of arsenious acid to 10 gallons of water.

After two applications, with an interval of twelve days between, viz., on July 16th and 28th, this crop also appeared to be somewhat damaged; but nevertheless the application was renewed on August 11th, 18th, and 21st, so that, on the whole, the solution was applied five times without preventing the crop from arriving at maturity.

A similar plot of ground, sown with turnips, was watered on the 3rd, 10th, 17th, and 27th of September, with a solution containing 1 ounce of acid to 10 gallons of water; so that, on the whole, 4 ounces of arsenious acid diluted with 40 gallons of water had been added.

Upon the turnips no sensible effect was produced by the application, the bulbs appearing as large, and the tops as luxuriant as they were in the rest of the bed which had not been so treated.

It may be worth remarking, although perhaps the circumstance might be owing to other causes, that the barley so watered arrived at maturity a fortnight earlier than the rest of the crop.

The produce was somewhat less than the average in the other

parts of the field, which in every 100 square feet was found to yield 12lbs. of straw, and 4lbs. 14 oz. of grain; the produce in the portion treated with arsenic being 10½ lbs. of straw, and 3½ lbs. of grain. The weight of the latter to the bushel was 52 lbs., whereas, that of the other portion was only 50 lbs.

The turnips from the arsenicated portion when arrived at maturity, yielded of

Roots	.. ..	51 lbs
Tops..	.. ..	20 „

whilst a similar portion of the same bed not treated with arsenic yielded

Of roots	.. ..	58 lbs.
Tops	.. ..	22 „

Thus much with respect to the influence of the poison upon the amount and quality of the production.

With the view of ascertaining whether these crops had really taken into their system any appreciable quantity of arsenic, the following method was adopted.

1st. With respect to the barley.

A portion of the grain was burnt in an earthen crucible, with plenty of nitrate of potassa, and the ashes were treated with hydrochloric acid. Sulphuretted hydrogen was then passed through the solution, but no precipitate was occasioned by its addition.

As however, it might be suspected that the arsenic had been driven off by the heat, notwithstanding the presence of nitre, by which it was intended to fix it, a second portion of the grain was heated in a glass retort for 5 hours together, with some nitro-hydrochloric acid. The liquor was maintained at a boiling temperature, and the vapour that came over, collected and tested with sulphuretted hydrogen as before.

In this instance, a slight precipitate was obtained, which afforded indications of arsenic by Marsh's test.

As however it was possible that a trace of this substance might have adhered to the external surface of the husk, from its having been sprinkled with the solution, a second portion of the barley was carefully washed before subjecting it to the same treatment, and here the indications were much less decisive, a very slight stain being perceived upon the subliming tube, but one of a reddish

colour, and less distinctly arsenical in its appearance than the former.

The suspicion thus created, as to the presence of arsenic in the case of the barley being merely superficial, was confirmed by my examination of the turnips, which had been similarly treated with an arsenical solution; for here the root, after being sliced into thin pieces and dried, was treated with a solution of chlorate of potassa, according to the plan recommended by Wöhler*, and the liquor, after filtration, subjected to the action of sulphuretted hydrogen. Here, as a dirty, greyish precipitate was thrown down, I might have suspected the presence of arsenic, but this presumption was overturned by the application of Marsh's test, which afforded no indications of arsenic whatever. I may also add, that Professor Brodie was good enough to submit another sample of the same turnips to chemical examination in his laboratory, but was unable to detect the presence of arsenic in it.

I also, on the 10th of last July, applied to a plot of similar dimensions with the former, containing a crop of barley, a solution of 4 ounces of nitrate of baryta in 4 gallons of water. The application was repeated on the 18th and 28th of July, and on the 11th, 18th, and 21st of August. No perceptible effect was produced upon the crop so treated, although the amount of grain was reduced from 4½lbs. in the 100 square feet, to 3¼ lbs. This, however, might be an accidental difference: for after a similar application to a crop of turnips, the weight of the roots somewhat exceeded the average of the crop in the rest of the same plot, weighing in 100 square feet 62 lbs., whilst the average of the remainder was 58 lbs.

Here the solution of nitrate of baryta was applied on September 3rd, 10th, 17th, and 27th, without any perceptible influence upon the character of the crop.

At the same time, similar experiments were made upon two corresponding crops of barley and turnips, by the application to them of 10 ounces of nitrate of strontia in 10 gallons of water, the application being renewed five successive times. No perceptible difference in either case resulted from the application in the character of the crop, and its amount in either instance seemed enhanced, but this might perhaps have been owing to other causes.—The following were the results obtained :—

* Hand-book, p. 218.

		In 100 square feet treated with strontian.	In 100 square feet not so treated.
Barley ..	Grain ..	5 lb. ..	4½ lb.
	Straw ..	16 „ ..	11 „
Turnips ..	Roots ..	53 „ ..	40 „
	Tops ..	13 „ ..	20 „

The barley and barley-straw, the turnip roots and tops, which had been watered with the above two solutions, were separately incinerated, their ashes reduced to whiteness by heat, then treated with nitric acid, and the solution evaporated to dryness and exposed to a red heat. They were then severally dissolved in hydrochloric acid and filtered. To the filtered solution sulphate of soda was added, and the precipitate formed was washed and dried.

Presuming the latter to consist of the earthy sulphates, I exposed each of them to a red heat for half an hour, mixed with an equal weight of carbonate of soda. The mass was then digested in water, and to the undissolved residue, muriatic acid was added.

So far the process was the same in all the eight cases; but to the hydrochloric acid solution, derived from the plants that had been watered with nitrate of baryta, after driving off the water, alcohol of specific gravity of ·810 was added. The salt derived from the grain of the barley was wholly dissolved by the alcohol: and was, therefore, inferred to consist entirely of chloride of calcium. That from the barley straw, as well as those from the turnip tops and roots, left, it is true, a slight residuum insoluble in the alcohol; but in only one of them, namely, that derived from the turnip tops, did the residuum, when dissolved in water, yield any precipitate with sulphate of soda; and, therefore, in that alone was the presence of baryta established.

Here then we are drawn to the same conclusion as in the case of the arsenic, namely, that the earth was not taken into the system of the plant, but had merely adhered to its external surfaces.

With regard to the other five solutions, which were derived from the ashes of plants watered with a solution of nitrate of strontia, after dissolving them in hydrochloric acid, and evaporating to dryness the solution obtained, they were severally treated with absolute alcohol like the former.

As, however, this menstruum takes up chloride of strontium as well as chloride of calcium, I trusted for the detection of the former earth to two tests, namely, first—the colour of the flame produced by setting fire to the alcoholic solution; and secondly—the effect of the addition to it of a weak solution of sulphate of soda. Now, in neither of these ways could I obtain any indication of the presence of strontia in the salt derived from the grain of the barley or from the roots of the turnips; but a slight precipitate was produced by the addition of sulphate of soda in the case of the barley straw and of the turnip tops, referable, as I conceive, to the same cause as the presence of baryta and arsenic in the foregoing cases, namely, to the adherence of a small quantity of the earthy salt to the external surfaces of the plant to which the solution had been applied.

I have trespassed upon the time of the Society in the detail of these experiments to a greater extent than I should have been otherwise disposed to do, out of consideration for those chemists who have arrived at conclusions opposite to my own; as it seemed but right to give to others ample means of judging, how far my experiments are calculated to shake their confidence in the results previously obtained.

The facts indeed which I have brought forward in this Memoir are, I must admit, too few in number, and, perhaps, too deficient in the required precision, to settle the question at issue; and I have consequently this very year commenced a similar set of experiments, in which I hope to have avoided the source of possible error which has been pointed out in those already undertaken,—namely, the adherence of some portion of the salt applied to the external surfaces of the stem and leaves of the plant, by introducing the salt into the soil before the seed is sown. I have also substituted the arsenic acid for the arsenious, conceiving that, being isomorphous with phosphoric acid, it has a better chance of being assimilated.

Whilst, however, I abstain from expressing a decided judgment as to the question at issue, I cannot help entertaining a confident belief, that as the results to which my experiments appear to point, seem more in accordance with the general principles of vegetable physiology than those opposed to them, further investigations will establish the fact, that whenever abnormal substances are taken up by a living plant, it is in consequence of some interference

with the vital functions of the roots, caused, in the first instance, by the deleterious influence of the agent employed.*

XIX. *On Colouring Matters derived from Coal Tar.*

By W. H. Perkin, Esq.

The subject of the present communication is one which is remarkable for the very rapid progress it is making. Previous to the year 1856, the colouring matters derived from "Coal Tar products" were practically unknown; but, owing to recent discoveries, they now rank amongst the most important colouring matters employed. Only a few of them, however, are actually used by the dyer and printer; the rest have merely a scientific interest, and for reasons presently to be mentioned, are not likely to acquire any other.

The coal-tar products which have up to the present yielded colouring matters are numerous. The following is a list of the most important, which are obtained either directly or indirectly from coal-tar:—

* In stating this as my belief, I do not pretend to pronounce what substances are to be regarded as abnormal either to vegetables in general, or to certain species in particular.

The late investigations, carried on by means of the spectrum, have shown, that even lithia is normally present in the ashes of tobacco; and, from the experiment of the Prince of Salm Horstmar, alluded to in p. 214, it might be conjectured that this alkali was present in plants generally.

Copper also was detected in them, as early as 1816, by Dr. Mupner (see Schweigger's Journal), and by Sarzeau, in eleven different kinds, in 1830. (Journal de Pharmacie.) These latter statements, indeed, have been called in question by Danger and Flandin; but they appear to be substantiated by the later researches of Dr. Odling, recorded in the "Guy's Hospital Reports, 1858."

The latter found copper in flour, in grain, in the straw of wheat and barley, in mangel-wurzel, and in Swedish turnips, as well as in a variety of animal substances. But the quantity discovered in these instances was so minute as to lend no countenance to the idea, that so large an amount of sulphate of copper as that taken up by plants in the cases reported by Saussure, could have found its way into their organism, if the vitality of the roots had continued unimpaired.

Aniline and its Homologues,
Carbolic acid,
Chinoline or Quinoline,
Naphthaline, and
Pyrrole bases.

1. *Aniline.*

ANILINE was discovered in 1826 by Unverdorben. The original method employed for its preparation was by digesting indigo with hydrate of potassium, and subjecting the resulting product to distillation. Aniline was also obtained from the basic oils of coal-tar. But the process which is now employed for its preparation is a remarkable instance of the manner in which abstract scientific research becomes in the course of time of the most important practical service.

Benzole was discovered by Faraday, who obtained it from oil gas. After this, it was produced by distilling benzoic acid with baryta, which result determined its formula, and was the cause of its being called benzole. After this, Mansfield found it to exist very abundantly in common coal-tar naphtha, which is the source from which it is now obtained in very large quantities.

Benzole, when studied in the laboratory, was found to yield, under the influence of nitric acid, nitrobenzole. Zinin afterwards discovered the remarkable reaction which sulphide of ammonium exerts upon nitrobenzole, converting it into aniline; and, lastly, Béchamp found that nitrobenzole was converted into aniline when submitted to the action of ferrous acetate. It is Béchamp's process which is now employed for the preparation of aniline by the *ton*. Had it not have been for the investigations briefly cited above, the beautiful aniline colours, now so extensively employed, would still be unknown.

When I discovered aniline purple, nitrobenzole and aniline were only to be met with in the laboratory. In fact, half a pound of aniline was then esteemed quite a treasure; and it was not until a great deal of time and money had been expended, that I succeeded in obtaining these substances in large quantities, and at a price sufficiently low for commercial purposes.

The colouring matters obtainable from aniline are numerous. They are the following:—

Aniline Purple.	Alpha-aniline Purple.
Violine.	Bleu de Paris.
Rosine.	Nitrazophenyline.
Fuschine.	Dinitraniline.

and Nitrophenylene-diamine.

Aniline Purple.

Generally known as Tyrian Purple, Mauve dye, Phenamine, Indisine, &c.

It has been known for many years that the hypochlorites react on aniline and its salts, producing a purple solution. In fact, hypochlorites are the distinguishing test for aniline; but nothing definite was known of the nature of this purple solution, it being simply stated that aniline produced with hypochlorites a purple liquid, but that its colour was very fugitive.

As many very absurd statements have been made respecting the discovery of aniline purple, I will just briefly mention how it was that I first became acquainted with it.

In the early part of 1856, I commenced an investigation on the artificial formation of quinine. To obtain this base, I proposed to act on toluidine with iodide of allyl, so as to form allyl-toluidine, which has the formula:—

$$\left.\begin{matrix} C_7H_7 \\ C_3H_5 \\ H \end{matrix}\right\} = C_{10}H_{13}N,$$

thinking it not improbable that by oxidising this, I might obtain the desired result, thus:—

$$\underbrace{2(C_{10}H_{13}N)}_{\text{Allyl-toluidine.}} + O_3 = \underbrace{C_{20}H_{24}N_2O_2}_{\text{Quinine.}} + H_2O$$

For this purpose, I mixed the neutral sulphate of allyl-toluidine with bichromate of potassium; but, instead of quinine, I obtained a dirty reddish brown precipitate. Nevertheless, being anxious to know more about this curious reaction, I proceeded to examine a more simple base under the same circumstances. For this purpose I selected aniline, and treated its sulphate with bichromate of potassium. This mixture produced nothing but a very un-

promising black precipitate; but, on investigating this precipitate, I found it to contain that substance which is now, I may say, a commercial necessity, namely, *aniline purple*.

The method adopted for the preparation of aniline purple is as follows:—Solutions of equivalent proportions of sulphate of aniline and bichromate of potassium are mixed and allowed to stand till the reaction is complete. The resulting black precipitate is then thrown on a filter and washed with water, until free from sulphate of potassium. It is then dried. This dried product is afterwards digested several times with coal-tar naphtha until all resinous matter is separated, and the naphtha is no longer coloured brown. After this it is repeatedly boiled with alcohol to extract the colouring matter. This alcoholic solution when distilled leaves the colouring matter at the bottom of the retort, as a beautiful bronze-coloured substance.

Before speaking further of the colouring matter, I will just describe the secondary, or, more properly, the primary products of the action of bichromate of potassium on sulphate of aniline, as nearly nine-tenths of the aniline employed in the preparation of aniline purple are converted into these useless substances.

These products are two in number, namely, the resinous matter which is separated from the black precipitate by means of coal-tar naphtha, and the residue which is left after the colouring matter has been extracted. The resinous matter, when separated from the coal-tar naphtha, consists of a brownish black pitch, which is fusible when heated. It is soluble in alcohol, ether, turpentine, bisulphide of carbon, and many similar solvents. It possesses one remarkable property, viz., that when its solutions in hydrocarbons are acidified with strong acids and well agitated, all the resinous matter is thrown out of solution and precipitated. Alkalies render it soluble again. These facts would make it appear to be a weak organic base.

This substance contains about 10 per cent. of nitrogen. It dissolves in fuming nitric acid, and by ebullition yields a yellowish brown acid. Anhydrous bichloride of tin, when heated with it, does not yield any colouring matter.

The residue which is left after the colouring matter has been separated is a purplish black powder. It contains about 30 p.c. of oxide of chromium. It is insoluble in all solvents, with the exception of strong acids, and is remarkable for the readiness with which it takes fire. It has been used for the manufacture of

black paint and printer's ink. As it contains large quantities of carbon and oxide of chromium, it would form a most valuable product for the preparation of anhydrous chloride of chromium.

The aniline purple prepared according to the process just described, although suitable for practical purposes, is not chemically pure. If required pure, it is best to boil it in a large quantity of water, then filter the resulting coloured solution, and precipitate the colouring matter from it by means of an alkali. The precipitate thus obtained should be collected upon a filter, washed with water until free from alkali, and dried. When dry it is to be dissolved in absolute alcohol, the resulting solution filtered, and then evaporated to dryness over the water bath.

Thus obtained, aniline purple appears as a brittle substance having a beautiful bronze-coloured surface; but if some of its alcoholic solution be evaporated on a glass plate, and viewed by transmitted light, it appears of a beautiful bluish violet colour. If considerable quantities of an alcoholic solution of the colouring matter containing a little water be evaporated to dryness, the surface of the colouring matter next to the evaporating dish, often exhibits a golden green appearance when detached.

Aniline purple is difficultly soluble in cold water, although it imparts a deep purple colour to that liquid: it is more soluble in hot water; but its hot aqueous solution, when left to cool, assumes the form of a purple jelly. It is very soluble in alcohols, though nearly insoluble in ether and hydrocarbons. Aniline dissolves it readily. In properties it seems to be slightly basic, as it is more soluble in acidulated than in pure water. Alkalies and saline substances precipitate it from its aqueous solutions as a dark purplish black powder. Bichloride of mercury precipitates it in a very finely divided state. A little of this precipitate (which appears to be a double compound of chloride of mercury and colouring matter) when suspended in water, and viewed by transmitted light, appears of a blue or violet colour.

A small quantity of hydrate of potassium or sodium added to an alcoholic solution of the colouring matter causes it to assume a violet tint, but without effecting any change in the colouring matter itself. Ebullition with alcoholic potash does not decompose it.

Aniline purple dissolves in concentrated sulphuric acid, forming a dirty green solution which, when slightly diluted, assumes a beautiful blue colour; excess of water restores it to its original purple

colour. It may even be heated for an hour to 100°C. with Nordhausen sulphuric acid without suffering decomposition, being restored to its original colour by means of water, and possessing precisely the same properties it had before being subjected to this powerful agent. Hydrochloric acid acts upon it in the same manner as sulphuric acid. It is decomposed by chlorine, and also by fuming nitric acid. Bichloride of tin is without action upon it.

Powerful reducing agents have a peculiar action upon this colouring matter, somewhat analogous to the action of reducing agents on indigo. An alcoholic solution of sulphide of ammonium mixed with an alcoholic solution of aniline purple, causes it to assume a pale, brownish tint. This solution, when brought in contact with the atmosphere, instantly recovers its original beauty and intensity of colour. An alcoholic solution of the colouring matter mixed with a little protoxide of iron, changes to a pale brown colour. This solution also becomes purple when exposed to the action of the atmosphere; sulphurous acid does not affect the colour of this substance.

Aniline purple forms a remarkable compound with tannin. When an aqueous solution of it is mixed with a solution of tannin, precipitation takes place. The precipitate thus formed after having been well washed, no longer possesses the properties of the pure colouring matter. It is insoluble in water. Like the pure aniline purple, it dissolves in concentrated sulphuric acid, forming a dirty green liquid; but on adding an excess of water to this solution, the new compound is precipitated unchanged; this compound is rather duller in colour than the pure colouring matter itself.

Aniline purple, when agitated with a little moist binoxide of lead, is transformed into *rosine*. It is remarkable for its intensity of colour, a few grains of it colouring a considerable quantity of spirits of wine.

Violine.—This colouring matter, which is a product of the oxidation of aniline, was first obtained by Dr. D. Price, who prepares it by heating an aqueous liquid containing two equivalents of sulphuric acid, and 1 eq. of aniline to the boiling point, and then adding 1 eq. of binoxide of lead, boiling the mixture for some time, and filtering it while hot. The filtrate, which is of a dark purple hue, is boiled with potash, both to separate the

excess of aniline, and also to precipitate the colouring matter; when all the free aniline has volatilized, the residue is thrown on a filter and slightly washed with water, and then dissolved in a dilute solution of tartaric acid. This solution, after filtration, is evaporated to a small bulk, re-filtered, and then precipitated by means of an alkali.

Thus obtained, violine presents itself as a blackish purple powder, which when dissolved in alcohol and evaporated to dryness, appears as a brittle bronze-coloured substance, similar to aniline purple, but possessing a more copper-coloured reflection. It is even less soluble in water than aniline purple. It is very soluble in alcohol, but insoluble in ether and hydrocarbons. Its solutions possess a colour somewhat similar to that of the field violet. Concentrated sulphuric acid dissolves it, forming a green solution, but excess of water restores it to its original colour.

The colour of violine, like that of aniline purple, is destroyed by reducing agents, but restored by the action of the atmosphere. Tannin produces an insoluble compound with it. When agitated with a small quantity of binoxide of lead, it is converted into aniline purple; excess of this re-agent changes it into roseine.

Roseine.—This substance almost always accompanies aniline purple, though in very small quantities. It was first noticed publicly by C. Greville Williams, and afterwards by Dr. D. Price. Williams used manganates for its preparation, but Dr. D. Price prepared it by means of binoxide of lead; his process is as follows. To a boiling solution of 1 equivalent of sulphate of aniline, 2 equivalents of binoxide of lead are added, and the mixture is boiled for a short time. The rose-coloured solution is then filtered, and the filtrate evaporated to a small bulk, which causes a certain amount of resinous matter to separate. This evaporated solution is then filtered, and the colouring matter precipitated by means of an alkali; it is then collected on a filter, slightly washed, and then dried. The colouring matter thus prepared readily dissolves in alcohol, forming a fine crimson-coloured liquid which, when evaporated to dryness, leaves the colouring matter as a dark brittle substance, having a slightly metallic reflection. It is much more soluble in water than either aniline purple or violine, but like them, it is insoluble in hydrocarbons, and more soluble in acid than in neutral liquids. Concentrated sulphuric acid dissolves it, forming a green solution;

excess of water restores it to its original colour. It forms a compound with tannin, and is also decolorized, or nearly so, by powerful reducing agents.

The three colouring matters just mentioned, viz., aniline purple, violine, and roseine, are evidently closely allied, for they have nearly the same properties. They are all formed under similar circumstances, namely, by the action of oxidizing agents in the presence of water. They are all slightly soluble in water, though, as the shade of colour becomes redder, so does their solubility increase. Alkalies precipitate them from their aqueous solutions. Concentrated sulphuric acid dissolves them all, forming green solutions, which excess of water restores to the original colour of the colouring matter; powerful reducing agents deprive them of their colour, (or nearly so), but it is restored by the influence of oxygen; and lastly, tannin forms insoluble compounds with them all.

Fuchsine or Magenta.—This beautiful product, which is often improperly called roseine, is a member of an entirely different series of compounds to the foregoing, being formed under very different circumstances, and possessing very different properties. It was first observed by Natanson, in 1856, when studying the action of chloride of ethylene on aniline, and afterwards (shortly before it was practically introduced into the arts), by Dr. Hofmann, when preparing cyantriphenyl-diamine by the action of bichloride of carbon on aniline. It was M. Verguin who first brought it forward as a dyeing agent, and who, I believe, taught manufacturers how to prepare it on the large scale.

Fuchsine is invariably formed at a temperature ranging from 170° to 190°C. It is produced from aniline, by the action of reducible chlorinized, brominized, iodized, or fluorized substances, as well as by weak oxidizing agents. The substances generally used for its preparation on the large scale, are the perchlorides of tin and of mercury, and the nitrates of mercury.

Preparation of Fuchsine by the action of Bichloride of Tin on Aniline.—Aniline combines with bichloride of tin, evidently producing a double compound; this product is a whitish substance, and may be prepared by adding to aniline bichloride of tin in the anhydrous state, or dissolved in water. Anhydrous bichloride of tin combines with aniline with great energy to form this compound.

To prepare fuchsine from the double compound, it is necessary

that it should be free from water, or nearly so: hence anhydrous bichloride of tin is generally employed for its preparation. The process adopted is as follows.—Anhydrous bichloride of tin is slowly added to an excess of aniline, the mixture being constantly stirred, and the pasty mass thus formed gradually heated. As the temperature increases, it becomes quite liquid, and also brown in colour. As soon as the temperature nearly approaches the boiling point of the mixture, it rapidly changes to a black-looking liquid, which, when viewed in thin layers, presents a rich crimson colour. This is kept at its boiling point some time, and then well boiled with a large quantity of water; by this means, the principal part of the colouring matter is extracted, together with considerable quantities of hydrochlorate of aniline. The residue is a solid, of a brown colour, and contains considerable quantities of tin in the form of a proto-compound.

The aqueous solution of the colouring matter and hydrochlorate of aniline is then boiled, so as to volatilize any free aniline it may contain, and then saturated with chloride of sodium. The chloride of sodium causes the colouring matter to separate as a semi-solid pitchy substance, of a golden-green aspect, while the hydrochlorate of aniline remains in solution. The colouring matter thus obtained may be further purified by digestion with benzole, which dissolves out a certain amount of resinous matter.

Preparation of Fuchsine by the action of Mercurous Nitrate on Aniline.—When mercurous nitrate is left in contact with aniline for some time, it forms a white pasty mass, but when carefully heated to 170°C. or 180°C., it reacts upon it, forming a brown liquid, which gradually changes to a dark crimson; at the same time the whole of the metal of the mercury-salt collects at the bottom of the vessel. This product, when separated from the metallic mercury, and allowed to cool, becomes semi-solid, being filled with crystals of nitrate of aniline.

To purify this product, it is best to dissolve out the nitrate of aniline it contains in a small quantity of cold water, and then to boil the remaining product several times with fresh quantities of water, until the principal portion of the colouring is extracted, and filtering the resulting aqueous solutions while hot. On cooling, these solutions deposit the colouring matter as a golden green tarry substance, from which benzole separates a small quantity of a brown impurity, leaving the colouring matter as a brittle solid.

I have briefly described the above processes, because they may, to some extent, be regarded as types of most of the methods employed for the production of this colouring matter, the first representing its formation by the action of reducible chlorides upon aniline, and the latter, by the influence of weak oxidizing agents upon aniline.

Fuchsine is undoubtedly an organic base, and a more powerful one than is generally supposed. The product obtained from aniline by means of bichloride of tin, is the hydrochlorate of fuchsine, and that obtained by the oxidizing action of nitrate of mercury is the nitrate of fuchsine.

Fuchsine is separated from its salts by precipitation with a small quantity of ammonia.

When freshly precipitated, it is a red, bulky paste, which, on drying, contracts to a purplish red powder. It is but sparingly soluble in water, though moderately soluble in alcohol; it is insoluble in ether and hydrocarbons. A small quantity of hydrochloric acid causes it to dissolve freely in hot water, but an excess of either hydrochloric or sulphuric acid dissolves it, forming a brownish yellow liquid, from which ammonia separates it unchanged; by this reaction it may be distinguished from roseine, which dissolves in strong sulphuric acid, producing the green liquid previously mentioned. Caustic alkalies, or ammonia in excess, partially precipitate fuchsine from its salts, but at the same time, dissolve a considerable quantity of it, forming nearly colourless liquids. Acetic acid added to these alkaline solutions restores the colour of the fuchsine, and if the liquids are concentrated, this base precipitates as a red floculent substance.

An alcoholic solution of fuchsine, when evaporated to dryness, leaves the colouring matter as a brittle mass, having a remarkably beautiful golden-green metallic reflection.

M. Béchamp has analysed carefully prepared specimens of fuchsine, and found it to have the formula: $C_{12}H_{12}N_2O$, the hydrochlorate being $C_{12}H_{12}N_2O,HCl$, and the hydrochloroplatinate, which is a purple precipitate, having the formula $C_{12}H_{12}N_2O,HPtCl_3$.

The existence of oxygen in this base is remarkable; because, in many instances, it is produced from agents which do not contain a trace of oxygen; as for example, bichloride of tin and aniline. The presence of oxygen in the product analysed, leads to the idea that it was a hydrate; thus—

$$\underbrace{C_{12}H_{12}N_2O}_{\text{Béchamp's fuchsine.}} = \underbrace{C_{12}H_{10}N_2}_{\text{Anhydrous fuchsine.}} + H_2O$$

This is perhaps, to some extent, confirmed by the fact that iodaniline when heated yields fuchsine:

$$2\,\underbrace{[C_6(H_6I)N]}_{\text{Iodaniline.}} = \underbrace{C_{12}H_{10}N_2}_{\text{Anhydrous fuchsine.}} + 2HI$$

But supposing the fuchsine examined by M. Béchamp, to have been a hydrate, it is remarkable that its hydrochlorate, and more particularly its hydrochloroplatinate, should also be hydrates. But, as our knowledge of this body is as yet but scanty, we must wait for the accumulation of facts before we can form any fixed opinion respecting its constitution.

The compounds investigated by M. Béchamp appear to be uncrystallizable. Sometime back I had upwards of a hundred gallons of a hot aqueous solution of this colouring matter, which had been prepared by means of nitrate of mercury. This solution, on standing until cold, deposited a considerable quantity of the colouring matter in the form of small octahedrons, having a most beautiful green metallic reflection.

Reducing agents decolorize fuchsine; but the oxygen of the atmosphere restores it to its original tint. If an alcoholic solution of fuchsine be left in contact with sulphide of ammonium until decolorized (or nearly so), and then exposed to the atmosphere, its colour is immediately restored; but if it be left to stand for several days, and then subjected to the atmosphere, several hours elapse before it assumes its original colour. Like aniline purple, fuchsine is a very intense colouring matter.

Tannin precipitates both fuchsine and its salts, forming difficultly soluble substances; bichloride of mercury also precipitates this base and its salts, forming double compounds.

When fuchsine is prepared by means of bichloride of tin, and more particularly when nitrate of mercury is used, there are two other colouring matters produced—one possessing an orange and the other a purple colour. It is on account of the presence of the former that some samples of commercial fuchsine possess a scarlet hue. Of this orange colouring matter scarcely anything is known. It is not precipitated from its solutions by alkalies. Of the purple

colouring matter also but little is known. It is formed at the same time as fuchsine, but in very small quantity, and is difficult to separate perfectly. Its properties are similar to those of fuchsine. It dissolves in concentrated sulphuric acid, forming a reddish brown solution, from which part of the colouring matter is separated by dilution with water. Hydrochloric acid dissolves it, forming a dirty yellowish-red liquid.

Bleu de Paris.—This is yet another colouring matter, produced under circumstances similar to those which give rise to fuchsine. MM. Persoz, V. de Luynes, and Salvétat give the following account of its preparation and properties:—

Nine grammes of anhydrous bichloride of tin and 16 grammes of aniline, heated for 30 hours to a temperature of about 180° C., in a sealed tube, produce neither a red nor a violet, but a very pure and lively blue. This blue, which resists acids, is darkened in colour by alkalies; but passes to a groselle violet when submitted to this agent in a concentrated state. It preserves its beauty of colour by artificial light, and it dyes animal fibres of a shade whose beauty leaves nothing to be desired.

This colouring matter crystallizes from its alcoholic solutions in fine needles, having an aspect similar to that of ammoniacal sulphate of copper. It is soluble in water, alcohol, wood-spirit, and acetic acid, but insoluble in ether and bisulphide of carbon. With concentrated sulphuric acid it forms an amber-coloured solution, which water converts into a magnificent blue liquid. Strong nitric acid decomposes it. Chromic acid precipitates it from its aqueous solutions without decomposition. Chlorine destroys it. Sulphurous acid does not decolorize it. I find that sulphide of ammonium is also without action upon it. It is precipitated from its aqueous solutions by alkalies and saline compounds.

Aniline-Green or Emeraldine.—Most chemists who have worked with aniline in the laboratory, must have noticed the peculiar green substance which forms on the outside of the various pieces of chemical apparatus which have been standing in the vicinity of any quantity of this body; this product is aniline-green.

Aniline-green has been known for several years. It may be formed by various processes. One process consists in oxidizing aniline with chloric acid. This is effected by mixing a hydro-

chloric solution of aniline with chlorate of potassium. It may also be obtained by oxidizing a salt of aniline with ferric chloride. Obtained by either of these processes, it presents itself as a dull green precipitate, which, when dried, assumes an olive green colour. It is insoluble in water, alcohol, ether, and benzole. Sulphuric acid dissolves it, forming a dirty purple-coloured solution, from which it is precipitated unchanged by water. With alkaline solutions it assumes a deep colour, somewhat similar to indigo; but acids restore it to its original tint. The colour of aniline-green is much enlivened by the presence of an excess of acid; but, unfortunately, as soon as this acid is removed, it passes back to its normal colour.

Toluidine, xylidine, and cumidine, yield colouring matters under the influence of oxidizing agents, and also when submitted to the action of reducible chlorides at high temperatures, analogous to those obtained from aniline under similar circumstances; but the results are generally not so good, the colour of the products becoming tinged with brown as the bases get higher in the series.

Nitrosophenyline.—This remarkable body is obtained by the action of nascent hydrogen on an alcoholic solution of dinitrobenzole. It is represented by the formula $C_6H_6N_2O$. It is almost insoluble in water, but soluble in acids and in alcohol, producing crimson-coloured solutions; but its colour is not nearly so brilliant as that of fuchsine. It seems gradually to decompose when kept. I have not tried any experiments with it as regards its dyeing properties.

Dinitraniline. — Dinitraniline is obtaind by decomposing dinitrophenyl-citraconimide with carbonate of sodium. When pure it crystallizes in yellow tables. It dissolves very sparingly in water, producing a yellow liquid. It has the formula

$$C_6H_5(NO_2)_2N.$$

It does not combine with acids or alkalies, although it appears to be more soluble in acidulated than in pure water.

Silk can be dyed yellow with dinitraniline.

Nitrophenylene-diamine, or Nitrazophenylamine.—Dinitraniline, when submitted to the action of sulphide of ammonium, changes into this beautiful base, which crystallizes in

red needles, somewhat similar in appearance to chromic acid. It dissolves in water, forming a yellow or orange-coloured solution, like that of bichromate of potassium. Alcohol and ether dissolve it freely. It is not at all like fuchsine in its properties, as it forms salts of a yellowish brown or grey colour, whereas, fuchsine forms crimson salts.

This base possesses the power of dyeing silk a very clear golden yellow colour.

Picric, or Trinitrophenic Acid.—This beautiful acid was discovered by Hausmann as early as 1788. It may be obtained by the action of heated nitric acid upon a great variety of substances. The following are the names of some of them :—indigo, aniline, carbolic acid, saligenine, salicylous and salicylic acids, salicine, phlorizin, cumarin, silk, aloes, and various gum-resins. It is now prepared for commercial purposes from carbolic acid, and also from certain gum-resins.

I have successfully prepared it from carbolic acid on the large scale in the following manner:—As strong nitric acid acts very violently when brought in contact with carbolic acid, I have found it best to use an acid having a gravity below 1·3, so as partially to convert the carbolic acid, and afterwards to boil it in stronger acid to change it into picric acid. On diluting the acid solution, the impure picric acid precipitates. To purify this further, it should be crystallized from boiling water.

When preparing this product for commercial purposes, it is advantageous to let all the nitrous fumes formed in its preparation, together with a certain amount of atmospheric air, pass over a fresh quantity of carbolic acid: this will absorb them, and, at the same time, be converted into nitro- or dinitro-phenic acid, and consequently diminish the quantity of nitric acid required for its manufacture.

In the preparation of picric acid from carbolic acid there is always a quantity of a yellow resinous matter produced, and at times a considerable quantity of oxalic acid. The latter is always produced when the acid which is used to finally convert the carbolic acid, is too weak: for then it rapidly decomposes the picric acid, yielding carbonic and oxalic acids.

Picric acid was introduced as a yellow dye about five or six years since by Messrs. Guinon, Marnas, and Bonney, eminent silk-dyers, of Lyons. Many of the cheap products sold of picric acid

are of a brown colour, and consist of impure di- and tri-nitrophenic acids, and sometimes of this crude product and ground turmeric.

Rosolic Acid.

Runge first noticed this substance in 1834, when studying creosote; but it was almost lost sight of, until again observed by Dr. Hugo Müller, only a short time since. He accidentally observed that when crude phenate of calcium is exposed to a moist heated atmosphere, as that of an ordinary drying stove, it gradually changes in colour, and assumes a dark red tint. This coloration is due to the formation of rosolate of calcium. (I have lately heard that phenate of sodium undergoes a similar change.) Dr. Müller's mode of preparing rosolic acid from this product, and his description of its properties, are given in his paper published in this Journal, vol. xi, p. 1; it is therefore unnecessary to repeat them.*

Mr. Duppa and myself, when investigating some of the derivatives of acetic acid, found that when phenic acid and bromacetic acid were heated together at 120°C., two products were formed, one possessing all the properties of rosolic acid, while the other had the character of brunolic acid. We also found that a mixture of iodine and carbolic acid, when heated with formic, acetic, butyric, or valerianic acids, produced rosolic acid or a similar substance. A mixture of carbolic acid and iodine did not give a similar result, but a black solid containing iodine.

Rosolic acid has lately been prepared on the large scale, and employed for the purpose of printing muslins. I believe it was the rosolate of magnesium that was employed for this purpose. I do not think it is now used, having been replaced by the more beautiful colouring matter, fuchsine. It was fixed by means of albumin.

Colouring Matters of Quinoline or Chinoline.

Chinoline is found associated with lepidine, cryptidine, and other of the higher nitrile-bases in the basic oils obtained from coal tar, and also in the products obtained by distilling cinchonine with caustic alkalies. It was previously termed *leucoline* or

* See also Tschelnitz (J. pr. Chem. lxxi: 416; and R. Angus Smith, Phil. Mag. (4) xiii, 45; Jahresbericht d. Chem., 1857, p. 447.

quinoline, but the substance described under these two names was found to contain three or more distinct bases. These have been studied by C. Greville Williams, who has applied the name *chinoline* to the product which forms the principal part of the impure substance originally termed quinoline. The substance used for the production of colouring matters need not be pure chinoline, as the product originally termed quinoline is of sufficient purity for this purpose.

Cinchonine appears to be the best source of chinoline, yielding, when distilled with excess of caustic alkali, 65 per cent. of this body sufficiently pure for manufacturing purposes.

Chinoline yields three colouring matters—a violet, a blue, and a green. The following is an account of their preparation by Greville Williams:—

In order to procure the blue colour, one part by weight of chinoline is to be boiled for ten minutes with one and a half parts of iodide of amyl. The mixture from being straw-coloured becomes deep reddish brown, and solidifies on cooling to a mass of crystals. This product of the reaction is to be boiled for ten minutes with about six parts of water, and, when dissolved, filtered through paper. The filtered liquid is to be gently boiled in an enamelled iron pan over a small fire, and excess of ammonia gradually added. The ebullition may be prolonged with advantage for one hour, the evaporation of the liquid being compensated for by the gradual addition of weak solution of ammonia. The latter may be prepared by the admixture of equal volumes of ammonia of density 0·880 and distilled water. The hour having elapsed the whole is allowed to cool, when the colour will almost entirely have precipitated, leaving the supernatant liquid nearly colourless. On pouring the fluid away (preferably through a filter, in order to retain floating particles of colour) the dish will be found to contain resinous looking masses which dissolve readily in alcohol, yielding a rich purplish-blue solution which may be filtered and kept for use.

The colour prepared as above is, as has been said, of a purplish tint, but if a purer blue be required, the following modification is to be resorted to. The filtered aqueous solution of hydriodate of amyl-chinoline is, as before, to be brought to the boiling temperature, but instead of adding ammonia, a solution of caustic potash, containing about one-fifth of its weight of solid potash, is to be substituted. The addition is to be continued at intervals until

three-fourths as much potash has been added as is equivalent to the iodine in the iodide of amyle used. The fluid may, after a quarter of an hour's ebullition, be filtered to separate the resinous colour. The product is a gorgeous blue with scarcely any shade of red. On adding the other fourth of potash to the filtrate while gently boiling, a black mass will be precipitated containing all the red, which otherwise would have been mixed with the blue. This mass dissolves readily in alcohol, yielding a rich purple solution, containing, however, an excess of red. The alcoholic solution on filtration leaves on the filter a dark mass soluble in benzole, and, as sometimes prepared, affording a brilliant emerald-green solution of great beauty. It is not always easy to obtain this green colour.

The properties of chinoline-violet and chinoline-blue are, as far as I have been able to ascertain, identical. They are resinous substances which present a coppery appearance by reflected light, but when in very thin layers, appear of a violet or blue colour by transmitted light. They are bases, and dissolve in acids, forming pale red solutions, which ammonia restores to their original colours. They are slightly soluble in hot water. Tannin precipitates them from their aqueous solutions, apparently forming an insoluble compound. Reducing agents do not affect their shade of colour.

Chinoline green is described by Greville Williams as having a brilliant emerald-green colour of great beauty. I have observed that when chlorine is passed through an alcoholic solution of chinoline blue, it changes into a green; but whether this is the green spoken of by Williams, I am unable to state.

Naphthaline Colours.

The beautiful hydrocarbon, naphthaline, which has yielded such a long category of substances to the chemist, has, up to the present time, yielded nothing of practical importance to the dyer. From it the following coloured derivatives have been obtained, namely, *chloroxynaphthalic acid, perchloroxynaphthalic acid, carminaphtha, ninaphthalamine, nitrosonaphthalin, naphthamein,* and a body of a purple *colour.*

Chloroxynaphthalic and Perchloroxynaphthalic Acids.—These acids were discovered by Laurent. They are produced by digesting their chlorides, namely, the chloride of chloroxynaphthyl and the chloride of perchloroxynaphthyl with an alcoholic solution of hydrate of potassium. They appear to be very difficult substances to obtain in quantity. I have not obtained satisfactory results when endeavouring to prepare them; they have the formulæ $C_{10}(H_5Cl)O_3$ and $C_{10}(HCl_5)O_3$ respectively. They are regarded with great interest, as being very closely allied to alizarine, the colouring matter of madder: in fact, they are viewed as chloralizaric acids; that hypothesis is based upon the idea of alizarine having the formula $C_{10}H_6O_3$; but it happens very unfortunately for this theory that the formula of alizarine itself is still a disputed point.

Chloroxynaphthalic acid is of a yellow colour; its salts are yellow, orange, or crimson, and are described as possessing great beauty. Silk dyed with the ammonium-salt acquires a good golden-yellow colour, little affected by light.

Carminaphtha.—This colouring matter was also discovered by Laurent. It is obtained by heating naphthaline with a solution of bichromate of potassium, and then adding sulphuric or hydrochloric acids. It is described as a fine red substance soluble in alkalies, but precipitated from its alkaline solutions by means of acids. I have never obtained this product when oxidizing naphthalene.

Ninaphthalamine.—Ninaphthalamine is the name given to a remarkable base which was noticed by Laurent and Zinin; but nothing was known of its nature until it was re-subjected to investigation by Mr. Wood, who has both described and analysed it and some of its salts; its formula is, $C_{10}(H_8NO)N$, or naphthalamine in which H is replaced by NO. It is obtained by passing sulphuretted hydrogen through a boiling solution of dinitronaphthaline in weak alcoholic ammonia. The details of the preparation are described in the 12th volume of this Journal, page 154. It has a bright red colour, but I do not think it would be of any value as a dyeing agent, even if it could be obtained cheaply.

Nitrosonaphthalin.—This peculiar body is a product of the

action of nitrous acid on naphthalamine. It is prepared by mixing a solution of hydrochlorate of naphthalamine with nitrite of potassium. From this mixture it separates as a redish-brown precipitate. This, when washed with water on a filter and then dried, is dissolved in alcohol, filtered, and evaporated to dryness on the water-bath. Thus prepared, it is a crystalline dark-coloured substance, having a greenish metallic reflection. It is soluble in alcohol and also in benzole, forming orange-red solutions.

When acids are added to an alcoholic solution of nitrosonaphthalin, it immediately assumes a most beautiful purple or violet colour as fine as any of the aniline purples. Alkalies restore it to its original colour. Silk may be dyed a beautiful purple shade with this substance, provided a certain quantity of hydrochloric or sulphuric acid be present; but what is most unfortunate is, that when the silk thus dyed is rinsed in water, the colour immediately passes back to that of pure nitrosonaphthalin, and, also, that the amount of acid required to keep up the purple shade, if left in the silk, rots it in a few days. Could this purple be fixed, nitrosonaphthalin would become a cheap and most useful dye.

I have endeavoured to produce a sulpho-acid of nitrosonaphthalin, thinking that if such a compound could be obtained, it would possess the purple colour, because it would be an acid itself. But although sulphuric acid does dissolve it, forming a blue solution, no combination takes place. I also endeavoured to produce this desired result by treating sulphonaphthalamic acid with nitrous acid, but obtained only nitrosonaphthalin, the acid of the sulphonaphthalamic acid having apparently separated.

Naphthamein.—Piria* observed that naphthalamine and its salts produce blue precipitates, afterwards becoming purple, when brought in contact with perchloride of iron, terchloride of gold, nitrate of silver, and other oxidizing agents. This product of oxidation he terms naphthamein. Silk and cotton may be dyed with it; but the colour of this compound is so inferior as to render it useless as a dyeing agent.

Naphthalamine, when heated with anhydrous bichloride of tin, yields a purple colouring matter, which is insoluble in water, but

* Ann. Ch. Phys. (3) xxxi, 217.

insolubility renders it difficult to use, and its colour is not nearly so good as that of aniline purple.

Tar Red.

This colouring matter was discovered by Mr. Clift, of Manchester, in 1853. It is obtained by exposing a mixture of the more volatile parts of the basic oils of coal tar and hypochlorite of calcium to the air for about three weeks. Of the pure colouring matter I know nothing, except that with tannin it forms an insoluble or difficultly soluble substance, and that with different mordants, it yields different colours.

Professor Calvert has been kind enough to send me a leaf of his Note-book containing the results of different experiments he made upon this colouring matter, which show that the colours obtained from this product are anything but good.

It seems probable that this colouring matter is derived from the pyrrole.

Azuline.

This substance, which is a beautiful blue dye, has been introduced into England within the last six months. It was discovered by Messrs. Guinon, Marnas, and Bonney, of Lyons, who keep the process for its preparation a secret. It is obtained from coal-tar; but from which of its numerous derivatives is not known.

This colouring matter is a brittle uncrystallizable body, possessing a coppery metallic reflection. It is very difficultly soluble in water, but soluble in alcohol, producing a magnificent blue solution, having but a slight tinge of red. With concentrated sulphuric acid, it forms a blood-red liquid, which when poured into an excess of water, precipitates the colouring matter unchanged. Dilute acids have no effect upon azuline. Its alcoholic solution mixed with an alcoholic solution of hydrate of potassium also changes to a dull-red colour. This, when diluted with water, forms a purple liquid, which is gradually restored to its original blue colour by hydrochloric acid. With excess of ammonia the solutions of azuline change to a reddish-purple colour. This is soluble in alcohol. I have made several experiments with it as a dyeing agent, but have not obtained any satisfactory results. Its

ammoniacal solution treated with sulphide of ammonium, gradually assumes a pale yellowish-brown colour. Iodine destroys the colour of azuline.

In colour it is not quite so fine as chinoline blue, though far superior to Prussian blue.

Application of Coal-Tar Colours to the arts of Dyeing Silk and Wool.

Silk and wool can be dyed with all the coal-tar colours, with the exception of the rosolates, these fibres possessing in most cases a remarkable affinity (if I may so speak) for these colouring matters. Many of them, as aniline-purple and violine, are taken from their aqueous solutions so perfectly by these substances, that the water in which they were dissolved is left colourless. In fact, silk and wool take them up so rapidly that one of the great difficulties the dyer has to contend with is to get the fibres dyed evenly.

Dyeing Silk with Aniline Purple, Violine, and Roseine.—One process is applicable for dyeing silk with either of these colouring matters, and it is a very simple one. The alcoholic solution of the colouring matter required is to be mixed with about eight times its bulk of hot water, previously acidulated with tartaric acid, and then poured into the dye bath, which consists of cold water slightly acidulated; after being well mixed, the silk is to be worked in it until of the required shade. If a bluer shade than that of the colouring matter is required, a little solution of sulphindigotic acid may be added to the dye-bath, or the silk may previously be dyed blue with Prussian blue or any other blue, and then worked in the dye-bath.

To Dye Silk with Fuchsine, Picric Acid, Chinoline blue, and Chinoline violet.—This process is still more simple than the above, as it is merely necessary to work the silk in cold aqueous solutions of these colouring matters. With fuchsine or picric acid, a little acetic acid may be used; but with chinoline colours, acids must be avoided. With picric acid, a very clear green colour may be obtained by adding a little sulphindigotic acid to the dye-bath.

I may mention that the colour of violine is not so fine as that produced by aniline purple and indigo blue; also that roseine is not so good a colour as fuchsine.

To Dye Silk with Azuline.—The dyeing of silk with this colouring matter is far more difficult than with the preceding, requiring to go through two or three different processes. This difficulty I believe arises from the unsolubility of azuline in water.

The process generally employed is to work the silk in a solution of the colouring matter in water acidulated with sulphuric acid, and when of sufficient depth, to raise the temperature of the dye-bath to the boiling point, and work the silk in it again; after this the silk is well rinsed in water, until free from acid, and worked in a bath of soap lather. It is then again rinsed and finished in a dilute acid bath.

To dye Wool with Aniline purple, Violine, Roseine, Fuchsine, and Chinoline colours.—This operation is generally conducted at a temperature of 50° or 60° centigrade, and the dye-bath is composed of nothing but a dilute aqueous solution of the colouring matter required. Acids should be avoided, or only a very small quantity used, as the resulting colours are not so fine when they are employed.

Methods of dyeing Cotton with Coal-tar Colours.

When Aniline purple was first introduced, considerable difficulty was experienced in dyeing cotton so as to obtain a colour that would resist the action of soap. Aniline purple is absorbed by vegetable fibres to a certain extent, and very beautiful colours may be obtained by simply working cotton in its aqueous solutions, but when thus dyed, the colours will not stand the action of soap. I have tried the use of tin and other mordants, but without any satisfactory result.

In 1857, Mr. Puller, of Perth, and myself, simultaneously discovered a process by which this colouring matter could be fixed upon vegetable fibres so as to resist the action of soap. This process is based upon the formation of an insoluble compound of the colouring matter with tannin and a metallic base in the fibre.

To effect this, the cotton has to be soaked in a decoction of sumach, galls, or any other substance rich in tannin, for an hour or two, and then passed into a weak solution of stannate of sodium, and worked in it for about an hour; it is then wrung out, turned

in a dilute acid liquor, and then rinsed in water. Cotton thus prepared is of a pale-yellow colour, and has a remarkable power of combining with aniline purple. The above process may be modified, as for example, the stannate of sodium may be applied to the cotton before the tannin, and alum may also be used in the place of stannate of sodium. To dye this prepared cotton with aniline purple, it is only necessary to work it in an acidulated solution of the colouring matter; when thus prepared, the cotton will absorb all the colouring matter of the dye-bath, leaving the water perfectly colourless. It has been found that cotton thus prepared can be dyed with any colouring matter that forms an insoluble compound with tannin. It is therefore used for dyeing with roseine, violine, fuchsine, and chinoline colours.

Cotton may also be dyed a very good and fast colour by mordanting it with a basic lead-salt, and then working it in a hot solution of soap, to which aniline purple has been added.

Oiled cotton, such as is used for dyeing with madder, is also used in dyeing these colours. Cotton simply oiled, and before mordanted with alum and galls, absorbs coal-tar colouring matters with great avidity, producing very fine shades. Oiled cotton mordanted with alum and galls also combines rapidly with these colouring matters: but as the colour of the prepared cotton, is generally rather yellow, it interferes sometimes with the beauty of the result.

Cotton is sometimes washed with albumin, which is coagulated by the action of steam, and the albumin, which covers the cotton, dyed in the usual manner.

I may mention that violine, roseine, fuchsine, and also the chinoline colours, combined with unmordanted vegetable fibres as well as aniline-purple. Picric and rosolic acids are not applicable for dyeing cotton.

Printing Calico with Coal-tar Colours.—The process generally employed for printing with these colouring matters is simply to mix them with albumin or lacterine, print this mixture on the fabric, and then to coagulate the albumen or lacterine by the agency of steam.

Mr. Grey, of the Dalmonach Print-works, and myself, discovered the first process of applying these substances to fabrics in a different manner to the above.

It consisted in forming a basic carbonate, or an oxide of lead, on

those parts of the cloth which were to be coloured, and then working the cloth thus prepared in a hot lather containing the colouring matter. Where the cloth was mordanted with the lead-compound, the colouring matter was absorbed; but where immordanted it was left white, because pure cotton is not dyed with these colouring matters in the presence of soap. This process was intended for the application of aniline-purple, for, at the period of this discovery, the other coal-tar colours were unknown. Colours dyed by this process were very pure; but it had many disadvantages which have caused it to be disused.

Lately the process previously described for dyeing colours upon cotton prepared with tannin, has been applied to calico-printing. It consists in printing tannin upon the fabric previously prepared with stannate of sodium, and then dyeing it in a hot dilute acid solution of the colouring matter (in the case of chinoline colours acid must not be used); by this means, the parts of the fabric which are covered with tannin are dyed a deep colour, but the other parts are only slightly coloured. These are cleared by means of well-known processes.

This method of applying these colouring matters is also modified by printing a compound of the colouring matter required and tannin on the prepared cloth, instead of the tannin only, and then steaming the goods.

Method of applying Aniline Green to Fabrics.—This process, which is interesting, as being the first example of the production of coal-tar colours on the fabric itself, was proposed by Professor Calvert: it is very simple. The design is to be printed on the cloth with a thickened solution of chlorate of potassium, dried, passed through a solution of an aniline salt, again dried, and allowed to hang in a moist atmosphere. In the course of two or three days, the colour will be fully developed. The colour thus produced may be changed into a dark blue by the agency of soap or an alkaline liquid. This process is very inexpensive; the amount of aniline required being very small.

Application of Nitrosonaphthalin.—If cloth is printed with a thickened solution of a salt of naphthalamine, dried, and then passed through a solution of nitrite of potassium, nitroso-naphthyline will rapidly make its appearance as a reddish-orange

colour; but unfortunately the colour thus obtained will not resist the action of soap.

Many of the coal-tar colours, when viewed by artificial light, are very much modified in tint; and some of them, when compared with similar colours of vegetable origin by daylight, appear of totally different tints by gaslight. The latter case is remarkably illustrated by aniline-purple and archil.

If two silk patterns are dyed, one with aniline purple, and the other with archil, of exactly the same shade of colour when seen by daylight, the colour of the archil pattern when viewed by artificial light, will appear several shades redder than that of the aniline purple.

Dr. Gladstone has examined solutions of these two colouring matters in a hollow wedge by means of the prism, and he finds that a very thin stratum of aniline-purple attacks the spectrum in the yellow (just beyond D), giving rise to a blue-purple colour; and that, as the intensity of the solution increases, the absorption gradually extends very slowly on the less refrangible side, but rapidly on the more refrangible side, till the green entirely disappears, and eventually the true blue.

In the case of archil, the violet and blue rays are absorbed by a strong solution of this colouring matter, though it still permits the extreme *red* ray to pass with great facility: therefore, considering the abundance of red in oil or gas-light, it is not surprising to find that archil colours appear redder by artificial light than those of aniline purple.

The colour of the three coal-tar blues, *bleu de Paris*, *azuline*, and *chinoline-blue*, when viewed by gaslight, are considerably modified. The *bleu de Paris* appears blue; azuline, a heavy blueish violet; while the chinoline-blue assumes a beautiful violet tint having rather a cast of red.

Dr. Gladstone has also kindly examined these three colouring matters, and gives the following account of his results:—These three blues, in common with aniline purple, attack the spectrum in the yellow (near D), and as the intensity of the colour increases, the absorption extends, especially on the more refrangible side, till the *green* is swallowed up. At the same time the *orange* is absorbed, while the extreme red is transmitted freely.

In the *bleu de Paris* there is an additional band of absorption in

the orange, when very weak solutions are examined; but this is soon merged in the greater band extending from the yellow as the solution increases in intensity.

Strong solutions of azuline absorb the yellow, green, blue, and violet in regular order; but the chinoline blue absorbs the violet when not very deep, and allows the blue to pass for some distance further, after which the *red* alone passes.

Dr. Gladstone states that the chinoline blue is one of the most beautiful dichromatic substances he knows; when viewed in a hollow wedge, with the prism, it passes gradually from a clear blue to a fine red.

Of the numerous colouring matters of which I have briefly spoken, there are only four that are at present employed by the dyer and printer; namely: aniline purple, fuchsine, picric acid, and azuline; but I think it probable that others of them will soon be introduced, such as the bleu de Paris. Nitrophenylene-diamine might also be used for silk-dyeing, as its colour is good, and it resists the action of light well.

Unfortunately the chinoline colours, though very beautiful, are most fugitive. There has been an endeavour to introduce the chinoline blue of late; but, although a considerable quantity of silk was dyed with it at first, it is now scarcely used, because, when exposed to the sun for two or three hours, the dyed silk becomes bleached.

Aniline purple resists the light best. Fuchsine and alpha aniline purple soon fade, especially when on cotton. Azuline and bleu de Paris are not easily acted upon by light when on silk.

When the colouring matters of coal-tar were first introduced, there was great fear that the workmen engaged in their manufacture would suffer in health. All I can say is, that during the few years I have had to do with this branch of manufacture, there has not been a single case of illness among the workmen that has been produced by any of the operations carried on for the production of *aniline purple*.

Researches on the Constituents of Gastric Juice.

By William Marcet, M.D., F.R.S.

In the spring of last year, being engaged with some investigations on gastric juice, I was induced to examine a sample of this secretion in Soleil's saccharimeter; when, to my astonishment, I observed it to act strongly on the polarized ray, rotating the plane of polarization of light to the left. I then undertook a series of investigations in order to determine which was the constituent of gastric juice possessed of the above optical property, and to what amount it exhibited this rotating power in the saccharimeter: these researches form the subject of the present communication.

The gastric juice used in my experiments was procured from two dogs, in whose stomachs I had established permanent fistulæ. One of these animals had been operated on in December, 1859; in the following month of October (1860), finding my supply of gastric juice insufficient, I established a gastric fistula in the second dog. The animals have both been in very good health ever since.

The gastric juice was obtained after allowing the dogs to fast for thirty or forty hours, and then feeding them with soft bones (*i.e.*, bones containing cartilage) boiled and cut up, or pieces of the windpipes of oxen or sheep—those of the ox being boiled (though not softened), the tracheæ of sheep being usually given raw. Windpipes were most frequently used, as they produced a good supply of the secretion, without causing any gastric disturbance. The secretion was collected from time to time during an hour or an hour and a-half after the animals had been fed, and from two to five ounces were usually obtained from each of them.

The fluid was in every case turbid when first extracted, containing, especially, fat. When the amount of substance in suspension was great, I found it advisable to begin by straining the gastric juice through calico; at all events, it had to be filtered through paper over and over again, until sufficiently clear to admit light freely through a layer of the fluid equal in thickness to the length of the saccharimeter-tube.

Every sample of gastric juice obtained under the above-mentioned circumstances from either of the dogs, rotated the plane of polarization of light to the left to an extent indicated by from 15° or 20° to 40° of Soleil's saccharimeter. The acidity of the

fluid, which was frequently determined, varied in 10 c.c. from 0·011 to 0·039 gramme—these numbers representing the amount of potash necessary to neutralise 10 c.c. of the gastric juice, equivalent to from 0·085 to 0·303 per cent. of hydrochloric acid. This degree of acidity, although rather lower, agrees with that obtained by Bidder and Schmidt (*Verdauungssäfte*, &c.), which is from 0·1708 to 0·3353 per cent. of hydrochloric acid.

My first impression was, that the optical properties of gastric juice were due to its acid. I therefore examined at once in the saccharimeter a sample of lactic acid prepared from sugar of milk; but it had no action on polarized light. Next, some lactic acid was extracted from flesh according to Liebig's process; this again exhibited no optical property in Soleil's polariscope.

After some consideration, I determined upon trying the separation of the constituents of gastric juice by means of hydrated oxide of lead, with the view of examining the action of light on the substances precipitated, and on those not precipitated, by this agent. Having boiled a sample of the secretion with hydrated oxide of lead in excess, and filtered the mixture, a fluid was obtained having a marked alkaline reaction, but containing only a comparatively small quantity of lead. I submitted this fluid to examination in the saccharimeter, and found it to act powerfully on polarized light. This proved that I had been mistaken in supposing that the action of gastric juice on polarized light was owing to its acid constituent.

Finding that the alkaline filtrate from the boiled mixture of gastric juice and hydrated oxide of lead contained the substance I was in quest of, I naturally believed it to be an alkali, and for a long while I endeavoured to isolate it under the form of crystals or of an insoluble salt. Failing in this, and finding that the substance was precipitated amorphous by alcohol, I determined upon availing myself of this means to prepare it in as pure a condition as possible; and, finally, I obtained a body having a definite rotating power on polarized light, and possessing the chemical properties of the substance known to result from the digestion of albuminous and gelatinous food, which Lehmann has called *peptone*.

Preparation.—The following is the process I adopted for the preparation of this substance, which, however, I could never obtain perfectly free from inorganic matters.

The gastric juice, excited, collected, and filtered as above, was boiled in order to coagulate the albumen (when, apparently,

according to Lehmann,* the pepsine is also precipitated), and then filtered, to be mixed with three times its bulk of commercial alcohol, 56 over proof (sp. gr. 842). A few hours later, or still better, the next day, the fluid was filtered from the *precipitate* which had formed, and then distilled or concentrated on the water-bath; the composition of the precipitate was subjected to a special inquiry. The residue from the distilled or concentrated fluid had a syrupy consistence; it was treated with a small quantity of sulphuric acid diluted with four or five times its bulk of water and added cold, the capsule containing the syrupy residue being at the time floated on cold water, to prevent any rising of temperature from the action of the acid; alcohol was next mixed with the thick acid fluid until the gelatinous precipitate it induced had ceased to increase, the mixture being at the same time agitated with a glass rod, to which much of the precipitate became attached. The gelatinous substance was now thoroughly washed with alcohol, and then dissolved in water, yielding a solution turbid from the presence of sulphate of lime, which had to be removed by filtration. I now boiled the clear fluid with an excess of hydrated oxide of lead, and after allowing the mixture to remain undisturbed till the next day, it was filtered. The filtrate was obtained clear, although on some occasions it had to be filtered repeatedly; it was then ascertained, with sulphuric acid and sulphide of ammonium, to be free from lead: it had an alkaline reaction, more or less strong, and contained a little lime with traces of soda-salts. I have succeeded, to a great extent, in getting rid of the lime, by adding cautiously to the fluid a very weak solution of oxalic acid, until it became nearly neutral, and then filtering. I also feel confident that the presence of a certain quantity of alcohol in the acid solution, previous to boiling it with oxide of lead, causes the precipitation of nearly all the lime as sulphate; indeed, I have quite recently ascertained that the acid solution in question, mixed with an equal bulk of alcohol, 56 o.p., in the course of two or three days, deposited the whole of its lime as sulphate; the fluid, after evaporation in order to get rid of the alcohol, giving no precipitate with ammonia and oxalate of ammonia, yet the amount of alcohol added had precipitated an insignificant quantity of the polarizing substance. In some instances I found the filtrate from the lead precipitate nearly

* Berichte über die Verhandlungen der Königlich-Sächsischen Gesellschaft de Wissenschaften zu Leipzig, 1849.

free from lime, which I attribute to the action of the alcohol which had remained mixed with the gelatinous substance after it had been washed with this fluid, or to all the lime having been precipitated at first by the addition of alcohol to the gastric juice: in these instances it was not necessary to use oxalic acid.

The alkaline filtrate from the lead precipitate, as free from lime as possible, was concentrated to the consistence of a thin syrup, and finally precipitated by alcohol, or a mixture of alcohol and ether. After a day or two the fluid, now become clear, was decanted, leaving a perfectly homogeneous substance, transparent, colourless, or nearly so, adhering to the sides of the receiver under the form of a thick, tenacious syrup, which was dried. The dry substance was very brittle, and exhibited no signs of crystallization; it could be easily scraped off from the sides of the receiver, from which it partly separated in scales; and, being very hygroscopic, had to be preserved in carefully-closed bottles.

Remarks on the above method of investigation.—In every case where gastric juice was obtained, as stated above, it yielded a precipitate by boiling. I made some experiments to determine whether the removal from gastric juice of the substance thus precipitated diminished its action on polarized light; but, on examining the fluid in Soleil's polariscope, before and after the precipitation, I could not discover any loss of its optical properties. When alcohol 56 o.p. (sp. gr. 842) is mixed with clear gastric juice obtained as stated above, which has been boiled and filtered, no turbidity or precipitate takes place until about an equal bulk of alcohol has been added. A further addition of alcohol causes a turbidity, and when the volume of mixture is equal to four times its original bulk, a cloudy precipitate gradually forms, leaving a clear fluid; but the next day the fluid may again have become turbid from the formation of a further quantity of the precipitate. This precipitate was collected on a filter, and, after being washed with a mixture of alcohol and water, was subjected to examination. I was surprised at finding it but partly soluble in water, yielding an acid solution; this solution acted, more or less, on polarized light, but much less than the original gastric juice, showing that some of the polarizing substance (if I may so call it) had been precipitated by the alcohol. For instance, a sample of eight ounces of gastric juice, showing 32·5° in the saccharimeter, being treated with three times its bulk of alcohol, gave a precipitate which exhibited in an aqueous solution measuring two ounces

13·5°; or a quantity of the polarizing substance in eight ounces of gastric juice, equivalent to 260°, lost a proportion equivalent to 27° by precipitation with three times its bulk of alcohol 56 o.p. This aqueous solution acting slightly on polarized light was also examined with respect to its inorganic salts; for this purpose, after evaporation to dryness, the residue was incinerated, and the ash was found to consist of phosphate of lime, with a little sulphate of lime: the addition of hydrochloric acid emitted no carbonic acid. I also examined the part of the precipitate insoluble in water, after it had been thoroughly washed with distilled water. It dissolved readily in gastric juice, but failed to increase its polarizing power. In one experiment, where I used the precipitate obtained from no less than fourteen ounces of gastric juice, and dissolved this in one ounce of the secretion showing 23°, this solution gave 24° when examined. As an increase of only 1° is not worth taking into account, it is obvious that the precipitate insoluble in water did not increase the optical property of gastric juice when dissolved in the secretion. The precipitate under our present consideration, insoluble in water, was incinerated, and I found it still contained a comparatively large quantity of organic matter. When burnt to ashes, this inorganic residue contained carbonates, as shown by the ready evolution of carbonic acid on the addition of hydrochloric acid,—although, previous to the incineration, no carbonic acid could be obtained; therefore, a carbonate had been formed by the ignition, showing that the precipitate had contained a compound of an organic and inorganic substance. The ash was found to consist of phosphate and carbonate of lime, with traces of sulphate of lime. On considering the organic substance precipitated by alcohol in gastric juice and insoluble in water, it appears to bear a great analogy to the *parapeptone* of Meissner, a substance discovered by this chemist among the products of digestion of albumen.* Parapeptone is obtained by neutralising with potash a solution containing hydrochloric acid and pepsine, after it has been used for the artificial digestion of albumen, this substance (parapeptone) being, under these circumstances, precipitated. It may be surmised that the compound of lime and parapeptone, when present in gastric juice, is precipitated by the addition of alcohol to the secretion, and then by filtration it will lose much of the acid which kept it in solution in the gastric juice, so that when washed with water, the aqueous fluid is no longer sufficiently acid to dissolve it, and, therefore, it

* Zeitschrift für Rationelle Medicin, series 3, vol. vii.

remains on the filter. I found this substance not only soluble in gastric juice, but also soluble in dilute acetic and hydrochloric acids, which bears out this view.

It will now be readily understood why I have in every case precipitated the gastric juice with alcohol, for by so doing I removed the whole, or, at all events, the greater portion of the parapeptone (if it be this substance), and also a quantity of phosphate of lime, which would have interfered, more or less, with the subsequent operations; although by so doing it was impossible to avoid the loss of a small quantity of the polarizing substance.

After freeing the solution from alcohol by distillation, and concentrating the fluid until it assumed a syrupy consistence, I added to it a very small quantity of a mixture of sulphuric acid with four or five times its volume of water. This was done with the view of transforming all the inorganic bases into sulphates, and setting free every organic and inorganic acid which might be present. By washing the gelatinous precipitate with alcohol, nearly the whole of the soda was removed; and on several occasions, especially during cold weather, I observed fine crystals of sulphate of soda in the alcoholic fluid a day or two later. If too much sulphuric acid was added to the syrupy fluid, the subsequent addition of alcohol failed to produce the gelatinous precipitate, when, of course, the whole operation was lost; in these cases, nothing more than a turbidity occurred. The formation of the gelatinous precipitate by the action of alcohol on the acid aqueous solution, and the washing of the precipitate with alcohol, was the cause of a considerable loss of the polarizing substance, which could not, however, be avoided.

The boiling with hydrated oxide of lead I believe to be indispensable to get rid of the sulphuric acid, the phosphoric acid, and other acids which had remained adherent to the gelatinous precipitate, and also perhaps of any pepsine which may have escaped precipitation in the former operations. By boiling the mixture for about three quarters of an hour, and then allowing it to remain undisturbed till the next day, it yields a filtrate which can be obtained quite clear with comparative ease, and perfectly free from lead; showing that the whole of the acids of the gastric juice have been removed, obviously from the formation of basic salts. It sometimes happens, however, that some sulphates escape the action of the oxide of lead, and find their way into the solution, which now only contains the polarizing substance, with a small quantity

of lime, soda, and sulphuric acid. I constantly found this solution more or less alkaline.

The treatment with oxide of lead is another source of loss of the polarizing substance; indeed, a large proportion of it remains in the lead precipitate. The following experiments show to what extent hydrated oxide of lead may precipitate the substance under consideration. Eight ounces of gastric juice were found to show 32·5° rotation in the saccharimeter; three times this bulk of alcohol was added, and the precipitate being the next day separated by filtration, was washed with water. This aqueous solution, measuring two ounces, was examined in the saccharimeter, and showed 13·5°. The alcoholic fluid was mixed with hydrated oxide of lead, and evaporated on the water bath to get rid of the alcohol; the next day this fluid was filtered, and the filter washed till the washings were no longer alkaline. The volume of the fluid amounted to 31½ ounces. I added half an ounce of water, and then examined the solution in the saccharimeter; it showed 7°. Now, if none of the polarizing substance had been lost by the evaporation in presence of oxide of lead, and subsequent filtration, the number of degrees found by observation in the saccharimeter ought to have been 10·6°, while, in fact, it was only 7°, a loss of about one third had, therefore, been experienced.

In a second experiment, a solution of the dry substance was prepared in 1½ ounce of distilled water, which showed in the saccharimeter between 15° and 15·5°. This solution was boiled for twenty minutes with hydrated oxide of lead, and again the next day for forty minutes; two days afterwards the fluid was filtered, and the filter washed with distilled water until the filtrate contained only a very small quantity of solid matters. The solution, concentrated to 1½ ounce, showed 11° in the saccharimeter; consequently about one-third of the substance had again been lost in the lead precipitate. As it might be objected, however, that the substance I am alluding to may possibly be decomposed by the mere boiling of its aqueous solution, and not taken up by the lead, I dissolved a sample of it in one ounce of distilled water, which solution showed 4·5° in the saccharimeter. The fluid was boiled for one hour, water being added to replace that which had evaporated; it was made up to one ounce, and examined, when it showed again 4·5°; consequently the substance is not decomposed under these circumstances. The next day the solution had become decidedly hazy, and the observation with the

saccharimeter more difficult; still it was seen to deviate the polarized ray to between 4° and 5°; consequently no appreciable amount of the substance dissolved had been decomposed by putrefaction, although the temperature of the air was very high during the whole of the experiment.

I found the polarizing substance to exhibit the chemical properties of Lehmann's peptone; they were as follows:—

Properties.—The substance when dry is brittle, non-crystalline, very transparent, and nearly colourless; it attracts moisture by exposure to the air, becoming a viscous mass. It is very soluble in water, and is precipitated from this solution by the addition of alcohol, and more completely so by a mixture of alcohol and ether. Its aqueous solution has the property of rotating the plane of polarization of light to the left. Four observations made, in order to determine the extent of this rotating power, with different weighed samples of the compound dissolved in 25 cubic centimetres of water, yielded, for 1° of Soleil's saccharimeter, 0·020 grm., 0·023 grm., 0·027 grm., 0·029 grm.; average 0·024 grm. Samples belonging respectively to the same specimens as those examined in the instrument were burnt in order to determine the weight of their ash; and this was subtracted from the weight of the corresponding substance employed for the determination of its optical properties. Therefore, 0·024 grm. of the substance under consideration, or a weight closely approximating to that dissolved in 25 c.c. of distilled water, gives 1° rotation to the left in Soleil's saccharimeter. I need hardly add that the action of a solution of the substance on the saccharimeter is perfectly proportioned to the strength of the solution; this, however, I determined by actual experiment.

The substance exposed to heat burns away almost entirely, leaving small and varying proportions of ash. With tannic acid, its solution yields an immediate and abundant precipitate; it is not precipitated by nitrate of silver, and bichloride of mercury induces in its solutions a slight turbidity. Neutral acetate of lead, in some cases, gave no precipitate; in others, precipitates more or less abundant were produced; these precipitates were evidently accidental, since, with some specimens, I failed to obtain a trace of turbidity on the addition of neutral acetate of lead; and in others the turbidity was but very slight. When this reagent had exerted no action, the addition of a few drops of ammonia to the solution of this salt, without impairing its transparency, caused a precipitate to appear

in the solution of the compound under consideration, just as in the case of peptone. Basic acetate of lead gave a precipitate which in most instances was soluble in an excess. I have recently obtained a sample of the polarizing substance which, when dissolved in water, yielded no precipitate with neutral acetate of lead, and with basic acetate of lead, a precipitate soluble in an excess, behaving, therefore, precisely like peptone. The aqueous solution is not precipitated by alkalies or mineral acids.

With respect to its chemical composition, the substance under consideration contains both nitrogen and sulphur. Dissolved in water, it readily undergoes spontaneous decomposition, especially in summer, when, after two or three days, the fluid becomes turbid, and shortly afterwards begins to emit a putrid smell.

In addition to this substance possessing the chemical properties of peptone, I may observe, that the method adopted for its preparation is precisely that which would yield peptone, and this substance must exist in gastric juice, unless every precaution be taken to obtain the secretion perfectly free from the products of digestion.

In order to control the above chemical results, and determine with every degree of certainty, whether the polarizng constituent of gastric juice is secreted in the stomach, or is actually a product of digestion, I have obtained gastric juice after washing out of the stomach all that it contained, and then again exciting the secretion by causing the dog to swallow fragments of bones from which the flesh had been carefully picked. On two other occasions, with the view of avoiding even the possibility of the substance given to the animal undergoing digestion, I used small silicious pebbles instead of bones. When the secretion was excited by fragments of bones, I obtained, in two experiments, samples of gastric juice which acted slightly on polarized light, both showing 7°. In my two experiments with the pebbles, I obtained no rotation at all; the secretion contained, therefore, none of the substance under consideration, proving thereby, that it is not secreted with the gastric juice, and consequently that its invariable presence in the animal fluid, when excited by means of wind-pipes or soft bones, must be the result of some process of digestion.

The next point of importance and interest was to ascertain which is the substance transformed in the stomach into polarizing peptone. I am engaged at present with this part of the investigation. So far, I have obtained proofs that cartilaginous structures, such as the trachea (oxen and sheep), and also bones

containing cartilage, yield, under the action of gastric juice, the substance in question. The following are the principal experiments from which this result is derived.

Experiment 1.—I excited the secretion of gastric juice by giving to one of the dogs some oxen's windpipe, boiled, but quite hard. The last quantities of gastric juice extracted were not mixed with the first; the first quantity, filtered, gave two ounces and four drachms, the second quantity six drachms, to which one drachm of the first quantity was added, in order to procure enough for the saccharimeter. The first quantity showed 32° rotation to the left, the second quantity showed 40°. It appeared, therefore, that the wind-pipe used for causing the secretion had been partly digested, and transformed into polarizing peptone; for if the optical properties of the fluid had been due to any other food which had remained in the dog's stomach since it had been last fed (although it was fasting at the time of the experiment), instead of having an increase of deviation from 32° to 40°, we should rather have expected a decrease of the rotating power.

Experiment 2.—The first and second quantities of gastric juice extracted in the preceding experiments were mixed together, the fluid showing 32°. (It ought to have been 34·5°. I cannot account for the discrepancy.) I took two quantities of the secretion, each measuring 1½ ounce, and placed them in two bottles of the same size; to one quantity I added 20 grammes of boiled wind-pipe cut up into small pieces, and both bottles were exposed for one hour to a temperature of 40° Centigrade, during which time the fluid containing the wind-pipe was frequently stirred. After an hour the mixture was filtered, when it appeared to me that the cartilaginous fragments had been partly dissolved, the edges having become somewhat rounded and worn off. The next day the filtrate was examined in the saccharimeter, when its action was found to be so powerful that the instrument was no longer available. In order to obviate this difficulty, I measured off 11 cubic centimetres of the gastric juice, and diluted it with an equal volume of distilled water. The diluted fluid was introduced into the tube of the instrument, and examined, when it showed 33° rotation. From this experiment, it is obvious that 1½ ounce of gastric juice, showing 32° rotation, after digesting 20 grammes of boiled oxen's trachea for one hour at a temperature of 40°, exhibited 66° rotation; its optical power had, therefore, increased to more than double; the polarizing peptone, which had been originally 3 per

cent., being, consequently, at the conclusion of the experiment, 6·3 per cent. of the gastric juice. The other sample of gastric juice, which had been used for the sake of comparison, showed 31° at the close of the experiment; the difference of 1° is so small, that it need not be taken into consideration.

Experiment 3.—One of the dogs, after fasting for forty-two hours, was allowed to eat fragments of hard bone cut up and perfectly free from flesh. A first supply of about two ounces of gastric juice was obtained under the influence of these hard bodies, and this was thrown on a filter. I then gave the dog some more pieces of bone, but these contained pieces of cartilage adhering to them, or were partly cartilaginous. The animal ate these greedily, and I obtained a second quantity of the gastric fluid, more abundant than the first; this was filtered separately, and yielded a fluid nearly as colourless as water. The next day I examined both samples of gastric juice in Soleil's polariscope. That obtained by the first process, *i.e.* after giving the animal bones free from flesh and cartilage, showed between 6° and 7° rotation; the samples extracted after the dog had eaten the bones and cartilage, showed between 17° and 18° rotation; it is, consequently, evident that the cartilaginous part of the bones had undergone digestion, and had increased, or greatly contributed to increase, the quantity of polarizing peptone from 0·6 per cent. to 1·6 per cent. of the gastric juice.

Finally, I may state that the residue of gastric juice obtained with wind-pipe or soft bones, contains a very large percentage of polarizing peptone. In one instance, where the indication in Soleil's polariscope was 31°, the proportion of the substance amounted to no less than 78 per cent. of the dry residue; and in another instance, where the gastric juice showed only 7° rotation, the proportion of this substance amounted to 32 per cent. of the dry residue. In these determinations a known weight of gastric juice was neutralized with a normal solution of potash, and then evaporated to dryness; the weight of the potash added was afterwards subtracted from that of the dry residue.

I have so far assumed that there is no other substance in gastric juice which rotates the plane of polarization of light; indeed, this appears to me satisfactorily shown by the investigations related in the present communication.

The following results are derived from my researches on the constituents of gastric juice.

1. That gastric juice, when its secretion is excited by means of soft (cartilaginous) bones, or the substance of wind-pipes, is invariably possessed of the property of rotating more or less the plane of polarization of light to the left.

2. That this optical property of gastric juice is due to its containing a substance exhibiting the chemical properties of Lehmann's *peptone*, a product of digestion; and 0·024 grammes of the substance, or a weight closely approximating to this, dissolved in 25 c.c. of water, rotates the plane of polarization 1° in Soleil's saccharimeter.

3. That gastric juice, when obtained after washing out the animal's stomach with water, and exciting its secretion by means of non-digestible bodies, such as silicious pebbles, exerts no action whatever on polarized light, thereby confirming the second conclusion.

4. That there is every reason to believe the above substance to be the only constituent of gastric juice possessed of the property of acting on polarized light.

5. That the substance to which gastric juice owes its optical properties is a product of digestion of the wind-pipes, or of the soft or cartilaginous bones used for exciting its secretion.

XXI.—*On the Peroxides of Potassium and Sodium.*

By A. Vernon Harcourt, Esq., F.C.S.
(student of christchurch.)

In 1810, three years after the discovery of the metals of the alkalies, the products of their oxidation were investigated by MM. Gay-Lussac and Thénard in France, and by Sir Humphry Davy in this country. These metals could then be obtained only in very small quantity. Sir H. Davy seems to have used in his experiments from one to eight grains, and MM. Gay-Lussac and Thénard employed a measured quantity which weighed no more than $\frac{3}{10}$ths of a grain. Another source of error in both sets of experiments was that the oxidation, instead of being allowed to proceed slowly, was suddenly effected at a high temperature by burning the metals in air or oxygen. It is probably to these two causes that we must attribute the fact

that these distinguished chemists failed to ascertain the constitution of the alkaline peroxides.

MM. Gay-Lussac and Thénard* give a table of the numbers which they obtained by burning a known weight of potassium in oxygen, and measuring the volume of gas absorbed. These numbers are in truth singularly discordant, and the authors draw from them no other conclusion than that "the potassium had combined with twice and even three times as much oxygen as it requires to pass into the state of potash." In three experiments they weighed the oxide formed, in order to prove that "whatever is the quantity of oxygen which potassium absorbs, the weight of the oxide is always equal to that of the potassium employed and of the oxygen absorbed, and therefore no volatile product is disengaged." In these three experiments, however, the weight of oxide formed, compared with that of the potassium employed, agrees with the supposition that this body is a teroxide. But it is plain from the expressions above quoted that the authors did not regard them as decisive of this point. With reference to the peroxide of sodium, they state similarly, as the result of their experiments, that "sodium can take up half as much oxygen again as it requires to pass into the state of soda, and even more." Sir H. Davy referring to this research says,† "I have been able to confirm in a general way these interesting results, though I have not found any means of ascertaining accurately the quantity of oxygen contained in these new oxides."

These extracts are sufficient to show that the definite statements as to the constitution of these bodies, which have found their way into most works on chemistry, and which are at variance with my conclusions, cannot rightly claim the authority of the great names which they allege.

The experiments of which I am about to give an account originated some time ago in the investigation of the action of carbonic oxide upon potassium made by Professor Brodie, under whose directions the earlier and more critical of them were performed. They have been conducted throughout in the laboratory of the University of Oxford.

The primary experiment consists in submitting a known weight of potassium or sodium to the regulated action of oxygen gas. It is necessary for this purpose that the metal should be pure, and

* Recherches Physico-chimiques, Tome i., p. 132.

† Bakerian Lecture, 1810.

have as clean a surface as possible; both that it may be accurately weighed, and because a crust of hydrate hinders the action of the gas. As its preparation in this condition requires some little care, and is thus essential to the success of the operation, it may not be out of place to describe the means by which it has been effected.

The potassium or sodium was first purified, shortly before being used, by filtration through linen. The arrangement finally adopted for this purpose consists of two tubes, of which the outer is a large and stout test-tube, about eight inches long and rather more than an inch in diameter; the inner is of the same length but one-third narrower, and open at both ends. Over one end of the inner tube, which is bent outwards into a lip, a piece of linen is tightly bound. This smaller tube should reach to within about an inch and a-half from the bottom of the larger, and it is secured in this position by passing through a cork which fits loosely into the outer tube. For a piston, I employ a cylindrical cork, which will pass, by gentle pressure, from end to end of the inner tube, and a stout glass rod for piston-rod. A small hole pierced in the cork permits the air to escape when the piston is being forced down, but does not allow the passage of the melted metal. When the apparatus is thus complete, it is half filled with naphtha, and the globules of potassium (or sodium, as the case may be,) are introduced into the inner tube. Ten or twelve grammes may conveniently be filtered at one operation in tubes of the size described. The temperature is carefully raised until the potassium fuses; the cork is then introduced and pressed gradually down upon the melted metal, which passes in a fine shower through the linen strainer to the bottom of the outer tube, and is perfectly freed from its coating of oxide. When the whole has cooled, the inner tube is removed, and the small metallic particles may be aggregated into globules of a convenient size by being again fused and judiciously stirred and pressed with a glass rod. In order to free from naphtha and introduce into the bulb, in which it is to be subjected to the action of the gas, a sufficient quantity of potassium at one operation, a number of these smaller globules, are cast into a cylinder. I employ for this purpose a glass tube, of about half an inch in diameter, and three inches and a-half in length, which has been closed at one end like a test-tube and then divided by a crack lengthwise, from end to end. The two halves are re-united for the operation by being

bound round with thread, and the mould thus formed is placed in a wider but rather shorter test-tube. It is then two-thirds filled with naphtha, which passes also into the outer tube, and the clean globules of potassium are rapidly introduced; by applying heat and stirring with a thin glass rod, the globules are readily united into one. In this way a solid cylinder of potassium is obtained, between one and one and a-half inch in length, and weighing from two to three grammes, which crystallizes on cooling with a brilliant metallic surface.

The apparatus used in the actual oxidation of the metal consists of a gas-holder of air and a gas-holder of oxygen; a washing bottle, containing solution of caustic potash, with which, by means of two separate tubes dipping into the fluid, both gas-holders communicate; a Liebig's bulb-apparatus, filled with the same solution; two U-tubes, containing respectively fragments of caustic potash, and pumice impregnated with strong sulphuric acid; a bulb of hard glass, in which the metal is exposed to the action of the gas; an air-bath for maintaining the bulb and its contents at a uniform temperature; and, lastly, a bulb-tube containing sulphuric acid, through which the gas passes as it issues from the apparatus. This bulb-tube (fig. 1) serves to close the

Fig. 1.

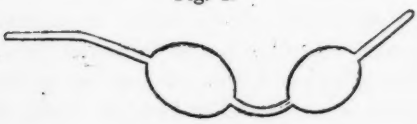


Fig. 2.

apparatus against diffusion, to mark the rate of passage and pressure of the gas, and to dry any bubbles of air which a too rapid absorption may draw back into the bulb. The capacity of the bulb itself (fig. 2) is about 150 c. c. It is provided with an india-rubber cork, through which two small tubes, bent at a right

angle, pass into its interior. These, when gas is to be transmitted, are connected by pieces of caoutchouc tubing, one with the drying apparatus, and the other with the bulb-tube. They are closed when the bulb is removed from the apparatus with plugs of india-rubber.

The first operation is to dry the bulb absolutely by connecting it with the apparatus, and heating it while a current of air is passed through. When cool it is again disconnected, closed by replacing the plugs in the delivery-tubes, and weighed. It is next filled with dry nitrogen, and again weighed. Meanwhile the split-tube in which the metal has been cast is transferred to a dish containing naphtha of a low boiling point, and the thread, with which it is bound together, is removed; the solid cylinder is readily detached on opening the mould, and may be washed for a moment in the fresh naphtha. It is then rapidly transferred, still covered with naphtha, to a tube through which a current of dry nitrogen is being passed; and the tube is immediately closed by a cork holding a piece of small tubing drawn out to a fine point. By the application of a gentle heat, the naphtha may be completely distilled off in the current of nitrogen. When this is effected, and the bulb is in readiness, the two corks are removed simultaneously, and the mouth of the bulb applied to the end of the tube; by depressing this end the cylinder of potassium is caused to glide, protected by the nitrogen, from one into the other. The cork with its glass tubes is replaced and the bulb and potassium weighed. I have never succeeded in bringing the metal into the bulb with its lustre unimpaired, owing, probably, to the presence of a trace of oxygen in the nitrogen used; but the undiminished sharpness of the lines of crystallization on the surface, and the dull metallic appearance which it still retains, seem to show that the superficial oxidation is quite insignificant. When the surface of the metal is dried with blotting-paper, an opaque white crust is formed, and a little naphtha always remains behind, however rapidly and carefully the operation is performed. The bulb is now placed in an air-bath, and re-connected with the drying apparatus before described; heat is applied, and when the metal is in a state of fusion, air is very slowly passed through. The point at which the action commences has varied in different experiments. With potassium it is generally rather above 100° C., and with sodium, about 200° C. In both cases, when the action

is once set up, it will continue at a much lower temperature, down apparently to the point of solidification of the metal.

The phenomena of the oxidation of potassium are remarkable.* Soon after the dry air has begun to mix with the nitrogen in the bulb, the grey film which covers the molten metal changes to a deep blue; the surface gradually becomes roughened by little wrinkles and projections, and a moment arrives when a single, spluttering spark appears at one point and a dust of white oxide rises in the bulb. At this instant the absorption begins. If very little oxygen is present in the bulb, the action is perfectly manageable, and the quantity of white oxide floating about is insignificant. But if the nitrogen has been replaced by air too quickly, a rapid absorption takes place, until the degree of dilution requisite for a gradual action has been attained, and a cloud of oxide covers the inner surface of the bulb, and passes, with each bubble of gas, through the sulphuric acid out of the apparatus. If, to obviate this, a plug of asbestos is placed in the exit tube, it becomes choked, and the transmission of gas is no longer possible. At the point at which the spark makes its appearance, the blue crust becomes white, and this change passes in a moment over its whole extent. Immediately afterwards it disappears entirely beneath the liquid metal, whose smooth surface is soon broken by innumerable projections which ascend and ramify with a steady, visible growth, having the white lustre of frosted silver. At the same time the metal climbs rapidly up the surface of the glass, extending in broad foliations, which grow together from side to side and cover sometimes the whole of the interior of the bulb. In more than one instance, the experiment has been abruptly terminated by this exuberant growth having reached to the delivery-tubes and stopped the passage of the gas. This phenomenon is probably due to the rising of the liquid metal by capillary attraction through the bulky powder which is being constantly formed upon its surface. At each point to which it thus ascends, it is converted into fresh oxide, which is flooded in its turn by fresh metal. After two or three hours, according to the rate at which air has been introduced, the whole becomes solid and the growth ceases. Gradually, as the oxidation proceeds, the metallic coating of the

* The changes which take place may conveniently be observed by using a beaker for air-bath during the first stages of the action.

inner surface of the bulb changes to a dead white, and the brilliant undergrowth crumbles down into a shapeless powder.

No one who has watched these changes can doubt that the action consists of at least two stages. By carefully regulating the heat and the supply of air, nearly the whole of the potassium may be converted into a white oxide. I have endeavoured, by discontinuing the action and weighing the bulb and its contents, to determine exactly the amount of oxygen which had been absorbed when this point was reached. But, in every case, before the dark metallic foliations had quite disappeared, some portions of the oxide had assumed the yellow colour characteristic of the final product. Two weighings made at this point render it probable that the white oxide is a binoxide; but I have never yet terminated the action at this stage and made an analysis of the product, because of the evident want of homogeneity above mentioned. Finally the temperature is raised, and oxygen transmitted in the place of air. Even at this point, the operation may be ruined by a too speedy admission of the pure gas; for great heat is produced by the rapid absorption thus set up, sufficient even to melt the oxide which has been formed; the glass is attacked, and the fused mass, having become impervious to the gas, is incapable of complete oxidation. The safest course is to employ air until nearly the whole is converted into yellow oxide.

The action is brought to a close only with difficulty, or at least after a long time. I give one example: -The weight of potassium in the experiment was 1·608 gms. The first weighing was made when the conversion into yellow oxide appeared to be effected.

Weight of bulb and oxide	.	.	.	.	29·2624
Do. after the passage of oxygen for	8	hrs.	at	210° C.	29·2924
,, ,,	4	,,		280°	29·3497
,, ,,	8	,,		230°	29·3645
,, ,,	4	,,		230°	29·3658
,, ,,	8	,,		230°—280°	29·3725
,, ,,	4	,,		270°—280°	29·373

The final product is a powder of the colour of chrome yellow. It cakes together when subjected for some hours to a temperature of 280° C., but may in great part be broken up within the bulb, and separated from the sides by gentle tapping and shaking. When exposed to the air, it rapidly absorbs moisture and gives off oxygen. It effervesces strongly on being thrown into water. It contains

four atoms of oxygen, and is represented by the formula K_2O_4.* The action of water upon it consists in the formation of two atoms of oxygen gas and one atom of binoxide of potassium, thus:—

$$K_2O_4 = K_2O_2 + O_2$$

I have ascertained the constitution of this body by determining, (1) the potassium which it contains, (2) the oxygen evolved from it by the contact of water and platinum black, (3) the oxygen evolved by the contact of water alone, and (4) the oxygen remaining in form of binoxide in the aqueous solution.

1.—*a.* 2·7665 grms. of potassium yielded 4·925 grms. of peroxide.

b. 1·6079 grms. potassium yielded 2·8779 grms. peroxide.

c. ·2946 grm. peroxide gave ·3648 grm. sulphate of potassium.

d. ·2276 grm. peroxide gave ·2765 grm. sulphate of potassium.

e. ·4495 grm. peroxide gave ·4481 grm. sulphate of potassium.

f. ·1414 grm. peroxide required for neutralization 7·07 c. c. of a standard solution of sulphuric acid, of which 1 c. c., according to a determination with chloride of barium, corresponded to ·01115 grm. potassium.

g. ·5093 grm. peroxide required 49·26 c. c. of a sulphuric acid solution, of which 1 c. c. corresponds to ·005682 grm. potassium.

2.—*a.* ·5844 grm. peroxide was introduced into a small apparatus contrived by Professor Brodie, consisting of a flask, in which the weighed amount of oxide is placed, together with, in these experiments, a small quantity of platinum-black, — a stoppered bulb, containing the fluid which is to be brought into contact with the oxide, and a potash-tube to dry the escaping gas. By loosening the stopper of the bulb, the water is suffered to descend upon the peroxide; a violent effervescence ensues. Five or ten minutes are generally sufficient to complete the action. The loss of oxygen in this experiment amounted to ·1894 grm.

b. ·584 grm. peroxide, treated in the same way, lost ·1825 grm. oxygen.

* O = 16; S = 32; C = 12.

3.—These experiments were made in exactly the same way as the last two, except that no platinum-black was placed in the flask.

a. ·4495 grm. peroxide lost ·0906 grm. oxygen.

b. ·2927 grm. peroxide lost ·0624 grm. oxygen.

c. ·5184 grm. peroxide lost ·124 grm. oxygen.

d. ·5291 grm. peroxide lost ·1098 grm. oxygen.

In *a*, the flask was immersed in a freezing mixture during the decomposition. In *b*, the water used was acidulated with sulphuric acid. Both methods were successful in preventing the decomposition of the solution of binoxide which is formed. In *c*, neither precaution was taken, and bubbles continued to rise through the fluid after the termination of the first action. The number representing the loss of oxygen is for this reason too high, and the binoxide remaining in the liquid, determined immediately afterwards with permanganate solution, was proportionately too low.

4.—*a.* ·2954 grm. peroxide, dissolved in water acidified with sulphuric acid, decolorized 54·39 c. c. of a solution of permanganate of potassium,* of which 1 c. c. corresponded to ·000595 grm. oxygen.

b. ·2049 grm. peroxide thrown into water containing ice, effervesced equally on the first contact, and decolorized 37·53 c. c. of the same standard solution of permanganate.

c. ·0899 grm. peroxide similarly treated, required 16·27 c. c. of permanganate.

d. ·0595 grm. peroxide required 10·8 c. c.

e. ·0614 grm. peroxide required 11·1 c. c. of a permanganate solution, of which 1 c. c. corresponded to ·000616 grm. oxygen.

These numbers, calculated on a hundred parts of the peroxide used, are compared below with those deduced from the atomic weight assigned to it.

		At. W.	p. c.	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
1.	K_2	78	54·93	56·17	55·87	55·51	54·45	55·86	55·8	54·96
	O_4	64	45·07							
	K_2O_4	142	100·00							

* This reaction has been ascertained by Professor Brodie to be perfectly definite, the two solutions losing exactly equal quantities of oxygen.

		At. W.	p. c.	*a.*	*b.*			
2.	K_2O	94	66·2					
	O_3	48	33·8	32·41	31·25			
	K_2O_4	142	100·0					
				a.	*b.*	*c.*	*d.*	
3.	K_2O_2	110	77·46					
	O_2	32	22·54	20·19	21·3	23·9	20·75	
	K_2O_4	142	100·00					
				a.	*b.*	*c.*	*d.*	*e.*
4.	K_2O_3	126	88·73					
	O	16	11·27	10·95	10·9	10·77	10·98	11·14
	K_2O_4	142	100·00					

I am sensible that numbers might be obtained, agreeing more closely than some of these do with the calculated results; but—regarding especially the ratio of the weights of oxygen in the three sets of determinations,—these seem to me already sufficient to leave no doubt as to the constitution of this peroxide.

The phenomena of the oxidation of sodium resemble, in some degree, those already described as occurring in the case of potassium. But they are far less striking. The growth upon the surface of the fused metal, in the first stage of oxidation, is lower and less tree-like; its lustre is soon dulled by a covering of white oxide. The metal does not spread itself on the glass, and in consequence a larger quantity may be operated upon at once in a bulb of the same size. I have several times employed Florence flasks for the oxidation of sodium; but they are always attacked to some extent by the oxide, which has more action upon glass than the peroxide of potassium at the same temperature. A shorter time and a rather lower temperature is required for the complete peroxidation of sodium than of potassium. The peroxide of sodium is of a pure white colour; like the oxides of zinc and tin, it becomes yellow when heated, and on cooling again loses this tint. Exposed to the air, it slowly deliquesces, and after a while resolidifies as carbonate. Great heat is produced on mixing it with water, and a small quantity of gas is evolved;* the quantity is least when the peroxide is in the state of fine powder, and is projected little

* This evolution of gas probably results from the local heating of the moistened peroxide: for the concentrated alkaline solution is rapidly decomposed at the boiling point.

by little into a large excess of acidulated water. If a small heap of it is moistened, it becomes yellow with heat, and the disengagement of gas is considerable. It contains two atoms of oxygen, and is represented by the formula Na_2O_2. The normal action of water upon it consists in the simple solution of the binoxide.

I have determined, in order to ascertain its constitution, (1) the sodium which it contains, and (2) the weight of oxygen which it loses by the contact of water and platinum-black, or when reduced by a standard solution of permanganate of potassium.

1.—*a.* 2·5225 grms. sodium yielded 4·2443 grms. peroxide.

b. 3·6418 grms. sodium yielded 6·1233 grms. peroxide.

c. 11·8085 grms. sodium yielded 19·79 grms. peroxide.

d. ·2861 grm. peroxide gave ·522 grm. sulphate of sodium.

e. ·4461 grm. peroxide gave ·8075 grm. sulphate of sodium.

f. ·3118 grm. peroxide required for neutralisation 28·1 c. c. of a standard solution of sulphuric acid, of which 1 c. c. corresponds to ·00658 grm. sodium.

g. ·352 grm. peroxide required 61·7 c. c. of sulphuric acid, of which 1 c. c. corresponds to ·003358 grm. sodium.

h. ·4132 grm. peroxide required 72·6 c. c. of the same acid.

2.—*a.* ·0979 grm. peroxide required, to impart colour to its solution, 31·6 c. c. of a solution of permanganate of potassium, of which 1 c. c. corresponded to ·00063 grm. oxygen.

b. ·1124 grm. peroxide required 42·75 c. c. of a solution of which 1 c. c. corresponded to ·000516 grm. oxygen.

c. ·0327 grm. peroxide required 8·4 c. c. of a solution of which 1 c. c. corresponded to ·000774 grm. oxygen.

d. ·1302 grm. peroxide required 33·46 c. c. of the same solution.

e. ·0715 grm. peroxide required 18·33 c. c. of the same.

The results per cent., derived from these numbers, are exhibited below :—

				a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
1.	Na_2	46	58·97	59·43	59·47	59·6	59·1	58·64	59·28	58·86	59
	O_2	32	41·03								
	Na_2O_2	78	100·00								

				a.	*b.*	*c.*	*d.*	*e.*
2.	Na_2O	62	79·49					
	O	16	20·51	20·33	19·64	19·88	19·89	19·84
	Na_2O_2	78	100·00					

Several experiments were made in the flask-and-bulb apparatus, before described, of the action upon the binoxide of water and platinum-black. The numbers arrived at agreed perfectly with those obtained in the determinations with permanganate of potassium.

When a solution of this binoxide of sodium is evaporated on a water-bath, oxygen is given off, slowly at first, but rapidly when the solid residue is beginning to separate. But if the evaporation is allowed to proceed slowly, at ordinary temperatures, by placing the solution under a bell-jar over sulphuric acid, large tabular crystals, of a hexagonal form, make their appearance.

These crystals are a hydrate of the binoxide of sodium. Their constitution was determined in the following manner:

When nearly the whole of the water had evaporated, the crystals were spread rapidly between two thick folds of blotting paper, round which a sheet of india-rubber was wrapped to prevent the access of carbonic acid. The whole was then strongly pressed for eight or ten hours.

In two preparations, the crystals thus dried were at once divided into two portions and analysed. One portion was dissolved in dilute acid, and the oxygen contained in it determined by a standard solution of permanganate of potassium. The other was placed in a silver boat and heated in a current of dry carbonic acid, by which the binoxide is readily converted into simple carbonate; the water which separates was collected at the same time in a weighed drying-tube. The increase in weight of this tube and the weight of the carbonate which has been formed, indicate at once the amount of water and of sodium which the hydrate contains. The following are numbers obtained in these analyses; they show that the crystallized hydrate consists of a combination of one atom of the anhydrous binoxide with eight atoms of water.

Preparation 1.—*a.* ·2546 gm. of crystallized hydrate required 29·72 c.c. of permanganate solution, of which 1 c.c. yielded ·0006116 grm. oxygen.

b. ·3968 grm. of hydrate gave ·1912 grm. carbonate of sodium, and ·2527 grm. water.

Preparation 2.—*a.* ·2350 grm. of hydrate required 26·82 c.c. of the same permanganate solution.

b. ·3614 grm. of hydrate gave ·176 grm. carbonate of sodium, and ·2305 grm. of water.

To place it beyond a doubt that the residue in these experiments consisted purely and simply of carbonate of sodium, it was washed into a flask, coloured with litmus, and determined by means of a standard acid solution. The results obtained were conclusive,—*e. g.*, ·176 grm.,—the weight of carbonate obtained in the last experiment,—required 22·72 c. c. of an acid solution, of which 1 c. c. corresponded to ·003358 grm. of sodium. This weight of pure carbonate of sodium ought theoretically to have required 22·74 c. c. of such a solution.

The percentage composition of this hydrate calculated from the foregoing data is compared below with that deduced from the formula assigned to it; the oxygen actually found being half that which the binoxide contains, its number is doubled:—

			Prep. 1.	Prep. 2.
Na_2	46	20·72	20·91	21·10
O_2	32	14·42	14·28	13·96
$8H_2O$	144	64·86	63·68	63·78
$Na_2O_2,8H_2O$	222	100·00	98·87	98·84

In a third preparation of the hydrate, the quantity of water which it loses when left to effloresce over sulphuric acid, was determined. The crystals, after having been dried as before, and weighed between watch-glasses, were exposed under a bell-jar over sulphuric acid, and re-weighed at intervals of two or three days. After nine days the weighings became constant, and the residue was determined as in the preceding experiments.

a. ·647 grm. of crystallized hydrate yielded ·3287 grm. of effloresced hydrate, and lost consequently ·3183 grm. of water.

b. ·2226 grm. of effloresced hydrate, heated in a current of dry carbonic acid, yielded ·2071 grm. of carbonate of sodium. The water given off weighed ·071 grm.

c. ·0268 grm. of effloresced hydrate, dissolved in acidified water, decolorized 5·98 c. c. of a solution of permanganate of potassium, of which 1 c. c. corresponded to ·0006116 grm. of oxygen.

The weight of water lost by the crystallized hydrate in Exp. *a*, corresponds to six out of the eight atoms which it contains. The

residue must therefore have the constitution Na_2O_2, $2H_2O$. Determinations *b* and *c* confirm this conclusion.

		Theory.		Found.
a.	$Na_2O_3,2H_2O$	114	51·35	
	$6H_2O$	108	48·65	49·2
	$Na_2O_2,8H_2O$	222	100·00	
b.	Na_2	46	40·35	40·37
	O_2	32	28·06	
	$2H_2O$	36	31·59	31·89
	Na_2O_2, $2H_2O$	114	100·00	
c.	Na_2O	62	54·38	
	O	16	14·03	13·65
	$2H_2O$	36	31·59	
	Na_2O_2, $2H_2O$	114	100.00	

It is worthy of remark that this hydrate stands in the same relation to a sesquihydrate and a protohydrate in which the binoxide stands to a sesquioxide and a protoxide. For if we subtract the formula of a protoxide from that of a sesquioxide, we obtain the formula of a binoxide; and similarly, by subtracting the formula of a protohydrate from that of a sesquihydrate, we obtain the formula of the hydrate of this binoxide:—

M_4O_3	$M_2H_3O_3$	$= \frac{1}{2}(M_4O_3 + 3H_2O)$
M_2O	$M\,H\,O$	$= \frac{1}{2}(M_2O + H_2O)$
M_2O_2	$M\,H_2O_2$	$= \frac{1}{2}(M_2O_2 + 2H_2O)$

Or again, as we compare a sesquioxide and the hydrate corresponding with a protoxide and its hydrate by the assumption of a distinct atomic weight, writing *e. g.* fe_2O, and feHO where $fe = \frac{2}{3}$ Fe, so the binoxide with its hydrate may, for the sake of a similar comparison, be represented by the formulæ na_2O and naHO, where $na = \frac{1}{2}$ Na.

The formation of these hydrates, together with the fact of the increased stability of a solution of peroxide when acidified, sug-

gested the expectation that corresponding salts might be obtained. Accordingly, three portions of a solution of binoxide of sodium were exactly neutralized with sulphuric, nitric, and hydrochloric acids respectively, and evaporated to dryness by exposure over sulphuric acid. The crystals which were formed consisted simply of sulphate, nitrate, and chloride of sodium. This experiment was repeated with the same result.

It has been stated that when the tetroxide of potassium is projected into water, a solution of binoxide is formed. It seemed probable that, by the slow evaporation of this solution, a hydrate might be obtained corresponding to the hydrate of the binoxide of sodium. Such, however, is not the case. Upon reaching a certain degree of concentration, the solution is entirely decomposed, with evolution of oxygen. The ultimate residue is opaque and slightly crystalline. It contains no binoxide.

The behaviour of these peroxides with various chemical reagents offers an interesting subject for investigation. I have already made a few experiments of this kind, a brief account of which I may be allowed here to append.

The general form of these experiments has been the same. The peroxide was placed in a boat of glass, silver, or platinum, and weighed in a small test-tube. The boat, with its contents, was then transferred to a piece of combustion-tubing connected at one end with an apparatus for drying the gas to be transmitted, and at the other with a bulb-tube (fig. 1) containing sulphuric acid. Heat was applied, as seemed requisite, by means of a lamp placed beneath the tube. When the action appeared to be complete, the boat and its contents were withdrawn, replaced in the test-tube, and again weighed. The operation was repeated a second time, or several times if necessary, until two successive weighings gave nearly the same result.

The first of these experiments consisted in heating the peroxides in an atmosphere of nitrogen, in order simply to ascertain their behaviour at a high temperature. 0·2288 grm. of binoxide of sodium were exposed in a silver boat to the strongest heat of a large Argand gas-burner. The powder passed from white to a full yellow, and caked together, but neither fused nor decomposed. The flame from a wire-gauze gas-burner, playing round the glass tube which contained the boat, produced partial fusion; at the same time, the silver was strongly acted upon, but no oxygen was

evolved. The temperature was then allowed to fall. The colour of the fused mass was black while hot, brown on cooling. It weighed ·2244 grm. On treating it with water, a quantity of oxide of silver separated, which was at the same moment reduced, with effervescence, by the excess of unaltered binoxide of sodium. Hence the only reaction which can be thus observed is that of the binoxide upon the silver: $Na_2O_2 + Ag_2 = Na_2O + Ag_2O$.

The tetroxide of potassium, similarly heated, became first of a deep orange colour, and then melted to a black fluid, which, when the temperature was allowed to fall, crystallized with shining tabular surfaces; the whole, on further cooling, gradually became yellow again. Its weight after it had been thus fused was unaltered. On applying the full heat of a large gas flame the black fluid was gradually decomposed with evolution of oxygen; the residue became grey and infusible. The loss of weight corresponded to a loss of two atoms of oxygen.

·504 grm. of tetroxide of potassium left a residue weighing ·3933 grm., or 78·4 per cent. If 2 atoms of oxygen are evolved, the proportion of the residue should be 77·47 per cent.

The weight of silver acted upon was ·597 grm., or rather more than $1\frac{1}{2}$ atom for 1 atom of peroxide. The action, whose completion the infusibility of the residue may have hindered, is doubtless the following:

$$K_2O_4 + Ag_2 = K_2O + Ag_2O + O_2.$$

From the fact that 2 atoms of oxygen were evolved while less than 2 atoms of silver were acted upon, it would seem to follow that the former action occurs independently of the latter.

Several attempts have been made, by bringing together sulphur and the tetroxide of potassium, to obtain the reaction,

$$K_2O_4 + S = K_2SO_4.$$

When these two bodies are heated together, a violent deflagration takes place; but by distilling the vapour of sulphur over the peroxide in an atmosphere of nitrogen, the action may be made to proceed gradually. In all the experiments, some sulphate was formed, and in one a large proportion; but, unless the temperature and the supply of sulphur vapour are most carefully regulated, the principal products are a polysulphide, of liver-colour, and sulphurous acid. Binoxide of sodium also readily combines with sulphur vapour, forming a brown fusible mass which contains a polysulphide and a little sulphate. Sulphurous acid is disengaged.

When binoxide of sodium is similarly heated in the vapour of iodine, the two gradually combine. The product is a white fusible body, apparently quite homogeneous.

·203 grm. of binoxide of sodium yielded ·8181 grm. of this substance; whence the amount of product corresponding to 100 parts of the binoxide is 403 parts.

According to the equation,

$$Na_2O_2 + I_2 = Na_2OI_2 + O;$$

100 parts should yield 405 parts. This equation represents in the simplest form the change of weight that has taken place, the substitution for an atom of oxygen of the equivalent quantity of iodine; but the residue may also consist of a mixture of iodide of sodium with iodite of sodium or iodate, *e. g.*:

$$3Na_2O_2 + 3I_2 = 5NaI + NaIO_3 + 3O.$$

On dissolving the product and adding an acid, a copious precipitate of iodine was formed. This iodine was determined, and the quantity found agreed with the conclusion above stated.

Action of Carbonic Oxide upon Binoxide of Sodium.

The dry gas, in this and the succeeding experiments, was slowly led through the tube in which the boat with its contents was placed, and the current from time to time discontinued; any absorption or evolution of gas could thus be readily noted by watching the movements of the fluid in the sulphuric acid bulb-tube (Fig. 1). At a temperature of 100°—150° C., a slight absorption took place. On raising the heat, it proceeded rapidly, a dark shade passing over the surface of the binoxide, which was at the same time partially fused. After a while, it again proceeded slowly, and the contents of the boat became once more white.

The weight of binoxide of sodium taken was ·352 grm.: the weight of the product ·4753 grm.; being in the ratio of 100 : 135.

According to the equation,

$$Na_2O_2 + CO = Na_2CO_3,$$

100 parts of binoxide of sodium should yield 135·9 parts of carbonate. The product was also identified qualitatively.

Action of Carbonic Acid upon Binoxide of Sodium.

At a temperature below 100° C. the first sign of action appeared. A shade of brown, as in the preceding experiment, passed over the binoxide, and at the same moment a slight absorption took place. On raising the temperature, after an hour's slow passage of the gas, a similar further action ensued. Finally the residue was perfectly white.

The weight of binoxide of sodium taken was ·4132 grm. that of the product ·5565 grm., being in the ratio of 100 : 134·7.

The product is, therefore, as before, carbonate of sodium; and the reaction which takes place is the following:

$$Na_2O_2 + CO_2 = Na_2CO_3 + O.$$

Action of Carbonic Oxide upon Tetroxide of Potassium.

The action was set up at a temperature of rather more than 100° C.; a single scintillation and a deepening of the colour of the peroxide marked its commencement. A weighed Liebig's potash-bulb apparatus and potash-tube had been attached to the apparatus, in order to determine the carbonic acid which it seemed probable might be formed. The even passage of the gas through the bulbs, while its action upon the peroxide was proceeding rapidly, showed that its volume suffered neither diminution nor increase. The residue in the boat, when the action was completed, was white. ·2314 grm. of tetroxide of potassium yielded ·2245 grm. of this product, numbers in the ratio of 100 : 97. 100 parts of the tetroxide should yield, theoretically, 97·2 parts of carbonate of potassium. The product was also identified qualitatively.

The potash-bulbs and tube gained only ·005 grm. In another experiment, where the gas issuing from the apparatus was passed through lime-water, no turbidity whatever was produced.

The reaction is, therefore, that expressed by the following equation:

$$K_2O_4 + CO = K_2CO_3 + O_2.$$

The perfect constancy in the volume of the gas throughout the experiment goes to prove, not only that the volume of oxygen

evolved is equal to that of the carbonic oxide absorbed, but that the two actions proceed proportionally. The carbonic oxide is substituted for an equivalent quantity of oxygen,

$$K_2O_2,O_2 + CO = K_2O_2,CO + O_2.$$

Action of Carbonic Acid upon Tetroxide of Potassium.

In the cold apparently no action took place, but it was set up below 100° C. The contents of the boat changed colour gradually from yellow to white. A quantity of oxygen was evolved. ·4498 grm. of the tetroxide yielded a product which weighed ·4379 grm. These numbers are in the ratio of 100 : 97·35. The product consisted of carbonate of potassium. The reaction is represented by the equation,

$$K_2O_4 + CO_2 = K_2CO_3 + O_3.$$

Action of Protoxide of Nitrogen upon Binoxide of Sodium.

The gas employed was prepared in the usual manner from nitrate of ammonium, washed with solutions of sulphate of iron and of caustic potash, and carefully dried. It had no action upon the binoxide until a temperature had been reached at which the latter showed signs of fusion, and of attacking the silver boat. At this point, a few particles became suddenly of a deep red, and this change passed by degrees upon the whole mass, which, though the heat was lowered, fused gradually with effervescence. A slight absorption took place, and the issuing gas lost for a while its power of brightening a glowing splinter of wood. The product was examined qualitatively. It had an alkaline reaction and gave off nitrous fumes in great abundance upon the addition of sulphuric acid.

A little of the substance had been thrown, by the effervescence which followed its fusion, out of the silver boat upon the sides of the glass tube in which it was placed. These spirtings were washed out, after the close of the experiment, and converted into chloride. The chloride thus formed weighed ·0791 grm. The

weight of binoxide of sodium originally taken was ·9068 grm.; which, after subtracting the weight of the amount lost, as deduced from the above determination, becomes ·8542 grm. The product, which was shown by the qualitative examination to consist principally of nitrite of sodium, weighed 1·4049 grm. These numbers are in the ratio of 100 : 164.

According to the reaction,

$$Na_2O_2 + 2N_2O = 2NO_2Na + N_2,$$

100 parts of binoxide of sodium should yield 176·9 parts of nitrite.

The alkaline reaction of the solution revealed one cause of the above deficiency, viz., the presence in the product of binoxide of sodium which had not been acted upon. The reaction might be due also to the presence of caustic alkali; but its formation under the above circumstances is exceedingly improbable, except through the action of the silver, and this action is insignificant in amount.

The phenomena of a second experiment exactly resembled those of the first; the absorption and the formation of nitrogen were well marked. There was again some loss by spirting, some action on the silver boat, and some alkali, presumably binoxide, remaining in the product. The error from these sources seemed more capable of being determined and thus eliminated, than of being avoided in any repetition of the experiment.

Accordingly, the spirtings were converted into sulphate and weighed; the amount of unchanged binoxide was determined by a standard acid solution; the silver boat was cleaned from oxide and its loss of weight ascertained; and, finally, the total amount of nitrite was determined by means of permanganate of potassium.

a. The sulphate formed from the spirtings weighed ·083 grm.

b. The solution of the total product required for its neutralization 10·4 c. c. of an acid solution, of which 1 c. c. corresponded to ·003376 grm. of sodium.

c. The same solution, largely diluted, and acidified, decolorized 305·6 c. c. of a solution of permanganate of potassium, of which 1 c. c. corresponded to ·0006116 grm. of oxygen.

d. The silver boat had lost by oxidation ·022 grm.

Hence we have,—		
Weight of binoxide originally taken . . .		·6047 grm.
Deduct—*a*. For loss by spirting .	·0456 grm.	
b. For unchanged binoxide	·0595 grm.	
Total . .		·1051 grm.
Weight of binoxide which has taken part in the reaction		·4996 grm.
Weight of the total product		·9491 grm.
Deduct—*b*. For unchanged binoxide	·0595 grm.	
d. For oxidation of the silver boat . . .	·0016 grm.	
Total . .		·0611 grm.
Actual product of the reaction . .		·888 grm.

·4996 : ·888 :: 100 : 177·7

A ratio closely coinciding with that calculated from the equation already given.

If we suppose the small quantity of binoxide of sodium reduced to protoxide by the silver of the boat to have remained in that condition and not to have been reoxidized by the protoxide of nitrogen, the ratio becomes 100 : 178.

The amount of nitrite calculated from determination *c*, after making a correction for the admixture of binoxide,* is ·859 grm. The deficiency was due to insufficient dilution causing the escape of a little nitrous gas.

Nitrous oxide does not act upon tetroxide of potassium at any temperature to which the latter can be heated without decomposition in a silver vessel.

Action of Nitric Oxide upon Binoxide of Sodium.

The gas was prepared by the action of nitric acid upon copper, washed in a large volume of water, and dried by passage through sulphuric acid. The apparatus was filled with nitrogen before the

* Nitrous acid is immediately oxidized by an acid solution of binoxide of sodium. Besides the source of error mentioned above, the determination of nitrous acid with permanganate of potassium is liable to the objection that the reaction towards the close of the experiment proceeds very slowly.

introduction, and again before the withdrawal, of the boat containing the binoxide, to prevent the formation of hyponitric acid. The first signs of action appeared at a temperature of about 150° C. Portions of the substance became of a deeper colour and began to fuse. The whole was by degrees converted into a clear colourless liquid, an absorption of the gas taking place throughout. ·6456 grm. of binoxide of sodium were taken: the product weighed 1·1396 grm. These numbers are in the ratio of 100:176·5. According to the equation

$$Na_2O_2 + N_2O_2 = 2NO_2Na.$$

100 parts of binoxide of sodium should yield 176·9 parts of nitrite of sodium.

Action of Nitric Oxide upon Tetroxide of Potassium.

From the analogy of the preceding reaction, it seemed probable that in this case a combination equally simple would lead to the formation of nitrate of potassium:

$$K_2O_4 + N_2O_2 = 2NO_3K.$$

This, however, is certainly not the principal reaction, and probably does not take place at all. In three experiments, the product consisted of a mixture of nitrate and nitrite of potassium. In the first, the two were formed in atomic proportions: the relation was probably accidental, since, in the succeeding experiments, the proportion of nitrite was larger. The action was set up either in the cold or upon the application of a gentle heat. The yellow colour of the peroxide changed to white in parts gradually, in parts after first assuming a deeper tint and undergoing semi-fusion. Copious red fumes were formed, which passed on into the bulb-tube (nitric oxide being all the while slowly transmitted,) and formed crystals with the sulphuric acid which it contained. At the same time, an absorption of gas was apparent. When no further change could be observed, the nitric oxide was expelled from the apparatus, as before, by a current of nitrogen, and the boat and its contents removed and weighed. A second exposure to the action of the gas at a higher temperature produced no change in the weight.

1.—·3735 grm. of tetroxide of potassium yielded a product weighing ·488 grm.

2.—·2633 grm. of tetroxide yielded a product weighing ·3394 grm.

3.—·3752 grm. of tetroxide yielded a product weighing ·4737 grm.

These numbers, referred to 100 parts of the tetroxide, become,

1.	2.	3.
130·6	128·9	126·2.

If the product consist of nitrite, 100 parts of tetroxide of potassium should yield 119·7 parts; if of nitrate, 142·3 parts.

The product of Exp. 1 was dissolved in water, and the solution was divided into three equal parts.

a. Part 1 was determined with a standard solution of permanganate, to ascertain the amount of nitrite in the product. It required 24·77 c. c. 1 c. c. of the solution corresponded to ·000561 grm. of oxygen.

b. Part 2 was mixed with sulphuric acid, evaporated, ignited, and weighed. The weight of the sulphate of potassium thus obtained was ·1533 grm.

c. Part 3 was introduced into a flask containing solution of caustic potash and fragments of zinc and iron. The ammonia evolved on boiling was collected and determined by means of a standard acid solution.* It required 11·5 c.c. of a solution, of which 1 c. c. corresponded to ·00204 grm. of nitrogen.

From *a*, the total product must contain ·2215 grm. of nitrite of potassium, and therefore, supposing it to consist entirely of a mixture of the two, ·2665 grm. of nitrate. The supposition may be tested by comparing the proportion of potassium and nitrogen which such a mixture should contain, with the results of the determinations *b* and *c*. ·2215 grm. of nitrite of potassium contain by calculation ·1016 grm. of potassium and ·0365 grm. of nitrogen; ·2665 grm. of nitrate of potassium contain ·1029 grm. of potassium and ·0369 grm. of nitrogen.

		b.	*c*.
Total potassium in mixture	·2045	·2062	—
Total nitrogen	·0734	—	·0707.

The products of Exps. 2 and 3 were similarly determined with the same result.

* The details of this method, which is both expeditious and exact, I hope to make the subject of a future communication.

Therefore, by the reaction of nitric oxide upon tetroxide of potassium, are formed hyponitric acid, and nitrate and nitrite of potassium in variable proportions. The only two palpable sources of variation are differences of temperature, depending upon the greater or less violence of the action, and differences in the time during which the hyponitric acid formed is in contact with the solid product, depending mainly upon the rate of transmission of the nitric oxide. The latter, I believe, to be the true cause of the variation in the product. If so, it is probable that three separate reactions play a part in producing the final result.

$$(1.)\ K_2O_4 + N_2O_2 = K_2O_2 + N_2O_4;$$
$$(2.)\ K_2O_2 + N_2O_2 = 2KNO_2;$$
$$(3.)\ K_2O_2 + N_2O_4 = 2KNO_3.$$

Long digestion, with a small quantity of nitric oxide, ought in this case to produce little but nitrate, and the action of a rapid current of the gas little but nitrite. Future experiments, especially upon the action of hyponitric acid on these peroxides, may decide this point.

XXII.—*Some Results of the Analysis of Commercial Coppers.*

By F. A. Abel, F.R.S.,

and

Frederick Field, F.R.S.E.

The influence undoubtedly exerted by such metals as antimony, arsenic, and bismuth, in modifying the physical properties of copper, renders their detection, with certainty, when present in minute quantities, and their correct estimation, of considerable importance. Although many processes have been suggested for the determination of these metals, and especially of the two first named, chemists of considerable experience and ability are frequently found to differ widely in the results of their analyses of commercial copper from the same source, one chemist insisting, perhaps, on the presence of arsenic in very appreciable quantities, while another denies its existence in the same sample.

The causes of these discrepancies are well illustrated by the circumstance that one of the methods for the separation of arsenic from copper, most generally recommended in all works upon analytical chemistry, even in the very latest editions,—namely, the digestion of their sulphides in the sulphides of ammonium, sodium, or potassium, has been shown, by the experiments of Mr. Bloxam, to be altogether fallacious, when the arsenic does not exist in greater proportion than one per cent.; and that even one part of that metal, in conjunction with ninety of copper, cannot be detected by that method.

When it is remembered that, in the superior classes of refined copper, arsenic is seldom found in larger quantities than 0·10 per cent., and frequently only in proportions of from 0·02 to 0·05 per cent., it is very evident that, by pursuing the course above alluded to, no arsenic would be dissolved by the alkaline sulphides, and, consequently, the absence of that metal would be presumed.

The separation of *antimony* from copper, by means of sulphide of ammonium, does not appear, from Mr. Bloxam's experiments, to be attended by the same difficulties as in the case of arsenic. Mr. Bloxam's researches upon this portion of the subject merely show that when 1 per cent. of antimony is present in copper the metal may be detected in the sulphide of ammonium-solution; but, with regard to smaller quantities than this, we have no information.* From many experiments which we have instituted, it would seem that the detection of less than three-hundredths of a grain in one hundred grains of copper cannot be relied upon with any degree of certainty.

It also appears, from the experiments of the same chemist, that 20 or 30 per cent. of *tin*, when alloyed with copper, may be overlooked when the separation is based upon the solubility of sulphide of tin in sulphide of ammonium.†

In the case of arsenic, when in combination with copper, far smaller quantities may, however, be detected than those stated by Mr. Bloxam, if hydrosulphuric acid is passed through the solution, to which ammonia has previously been added, in excess. By

* Quarterly Journal of the Chemical Society, Vol. v. p. 104.

† In a note (p. 370) appended to the last edition of Fresenius's Quantitative Analysis, the author says that M. Lucius, one of the students in his laboratory, has succeeded in effecting the complete separation of copper from tin, by means of yellowish sulphide of sodium, but it is indispensable to digest them three or four times with sufficiently large quantities of the solvent.

adopting this method of operating, the arsenic is never precipitated, and consequently the separation is nearly, if not quite, complete. It is only necessary to saturate thoroughly with hydrosulphuric acid, in order to prevent traces of copper from entering into the ammoniacal liquid. For example :—

In a mixture of 10·00 grains of copper
and 0·10 grain of arsenic,

the latter was immediately detected, on the addition of hydrochloric acid to the filtered liquid.

In 10·00 grains of copper
mixed with 0·01 grain of arsenic,

the latter was discernible when the filtrate, mixed with excess of acid, had been kept in a warm place for half an hour.

Arsenic may, moreover, be detected in copper, in quantities not less than 0·20 to 100·00 of the latter, when the mixed sulphides are digested in strong sulphide of ammonium for many hours.

Although the rules laid down in analytical works, for the detection and separation of nearly every metal with which we are acquainted, appear, generally speaking, to be sufficiently plain and conclusive, every chemist must have experienced the difficulty of separating, or even distinguishing, very small quantities of metals, when associated with another in very much larger proportion. To take for example, the examination for tin, antimony, arsenic, and bismuth, of a specimen of refined copper which is supposed to be nearly pure, having passed through the various stages of its metallurgy, until the completion of the final operation. The copper would be dissolved in nitric acid, and water added; when, in the majority of cases, a turbidity in the liquid would be thereby produced. This might consist of antimonious or antimonic acid; arsenic, as arseniate of antimony; bismuth, thrown down from its solution as basic nitrate; lead, as sulphate (for if a trace of sulphur is present, sulphuric acid will be formed, and sulphate of lead consequently produced); and the whole of these compounds may weigh collectively only two- or three-tenths of a grain. Should either the nitric acid or water employed contain a trace of chlorine, silver, which is almost invariably found in copper, would also be separated, and add to the complexity of the precipitate.

Having ourselves individually experienced numerous difficulties such as those glanced at above, in the constantly recurring exa-

mination of specimens of commercial copper, we have devoted considerable attention to the improvement of the existing methods for the detection and correct estimation of its metallic impurities, and especially of antimony, arsenic, and bismuth; and in our researches on this subject we have, with the valuable co-operation of Mr. E. O. Brown, arrived at results which we believe are sufficiently important to analytical chemists, to warrant their publication.

The following is a method which, after various modifications, we have now employed for some time, with considerable success, both for the quantitative and qualitative examination of copper, when antimony, arsenic, bismuth, and lead, have to be detected and estimated.

About 200 grains of the metal are dissolved in nitric acid, a small quantity of solution of nitrate of lead is added, equal to about 10 grains of the salt, and subsequently an excess of ammonia and carbonate of ammonia. A precipitate is formed, which may consist of oxide and carbonate of lead, arseniate and antimoniate of lead, and oxide of bismuth, the whole of the copper remaining in solution. The precipitate is separated by filtration, thoroughly washed and digested in a strong solution of oxalic acid, whereby the antimony and arsenic are dissolved.

To the filtered liquid, sulphide of ammonium is added, or, what is preferable, it is rendered alkaline by ammonia, and hydrosulphuric acid is passed through to saturation. Traces of sulphide of copper generally impart a brownish tinge to the liquid, and are deposited after some time, as it is nearly impossible to wash away the last traces of that metal from the nitrate of lead-precipitate. This sulphide is filtered off, and a slight excess of hydrochloric acid is then added to the filtrate, which is diluted to about 8 ounces. If any large amount of either antimony or arsenic be present, there will be an immediate precipitate. If smaller quantities exist (one- or two-hundredths of a grain) the flask should be placed on the sand-bath for a few hours, and the temperature maintained at from 140° to 200° Fahr., when the metals, if present, will make their appearance as sulphides. If the precipitate be orange or orange-red, the presence of antimony is certain, but if of a pure canary-yellow, its absence may be presumed.

The precipitated sulphides are oxidized by means of concentrated nitro-hydrochloric acid, the clear solution is mixed with chloride

of ammonium and excess of ammonia, and the arsenic is separated as the ammonio-magnesian arseniate ($2MgO, NH_4O, AsO_5, HO$). The filtrate from this is slightly acidified with dilute hydrochloric acid, and the antimony is precipitated by hydrosulphuric acid, and ultimately determined as antimoniate of teroxide of antimony (SbO_4). Should the presence of antimony and arsenic have been previously ascertained, it is, of course, unnecessary, in the quantitative process, to precipitate them both as sulphides from their solution in oxalic acid, as the arsenic may be at once precipitated by the addition of sulphate of magnesia and excess of ammonia, and the antimony determined in the filtrate.

In the determination of the *bismuth* and *lead* contained in copper, uniformly successful results have been obtained by employing the following method, which, as far as regards the separation of these metals from the copper and from any tin, antimony, or arsenic that it may contain, is founded upon the plan for detecting the arsenic and antimony just now described.

The nitric acid-solution of about 200 grains of the copper, is mixed with a small quantity of solution of phosphate of soda; ammonia in excess is then added; and the resulting precipitate is collected and purified from copper by washing with ammoniacal water. This precipitate is afterwards dissolved in hydrochloric acid, its solution is rendered alkaline with ammonia, and submitted to a current of hydrosulphuric acid. The precipitated sulphides of lead and bismuth are thoroughly washed, and dissolved in dilute nitric acid; the solution is nearly neutralized with ammonia, and then digested with a little hydrated oxide, or basic nitrate, of copper, which precipitates the oxide of bismuth, while lead remains in solution. The precipitate is thoroughly washed, dissolved in dilute nitric acid, and the bismuth separated from the copper by the addition of excess of ammonia; the oxide of bismuth thus obtained is purified by washing, and its weight determined in the usual manner. The solution containing the nitrates of lead and copper is mixed with solution of carbonate of soda; excess of acetic acid, and a small quantity of bichromate of potassa are added, and the chromate of lead is collected.

It should be observed that, in the event of the copper containing iron, that metal would be obtained as oxide together with the bismuth. When this is the case, which may readily be known by the brownish tinge imparted to the oxide of bismuth, they have to be separated. The mode of operation does not need description here.

The analytical methods just described are available not only for the determination of appreciable quantities of the metals antimony, arsenic, bismuth, and lead, but also for the detection of very minute proportions of those metals, and especially of the first two, when existing in copper.

In order to test the delicacy of the method described for the detection of minute traces of either arsenic or antimony, the following experiments were instituted:—

100 grains of electrotype-copper were dissolved in nitric acid, nitrate of lead was added, and afterwards a mixture of ammonia and carbonate of ammonia; the precipitate was boiled with solution of oxalic acid for half an hour, the dissolved portion filtered, and sulphide of ammonium added in excess. The few black flakes of sulphide of copper were separated by filtration, and hydrochloric acid was added to the filtrate. An opalescence was produced, which did not increase upon the application of gentle and long-continued heat, and did not assume any tinge of yellow: arsenic and antimony were therefore presumed to be absent.

Another 100 grains of the same copper were dissolved in a similar manner, and 0·1 grain of arsenic acid was added to the solution. The precipitate with nitrate of lead and carbonate of ammonia, treated as described above, gave an instantaneous indication of arsenic, which increased very much upon applying heat, the sulphide falling down in clear yellow flocks. Another similar quantity of the copper was tested with the addition of 0·05 grain of arsenic acid. The result was not so instantaneous, but, eventually, equally conclusive. 0·02 grain was then tried, with a similar confirmation; and even 0·01 grain of metallic arsenic, when dissolved in nitric acid, and added to the solution of the 100 grains of metallic copper, became, after some time, abundantly evident.

From these experiments, it appears that there is no difficulty whatever in detecting minute traces of arsenic in the presence of copper, the latter existing, in proportion to the former, as ten thousand to one.

A similar series of experiments was made upon the detection of antimony by this method. 0·10, 0·05, 0·02, and 0·01 grain were each added to four solutions of 100 grains of copper in nitric acid, and the results were quite as satisfactory as in the case of arsenic.

The presence of arsenic, even in a very small quantity of commercial hydrochloric acid, can be easily detected by this method. If a few drops of the acid be added to an ounce of water, nitrate of lead and excess of ammonia introduced, and the precipitate digested in sulphide of ammonium, the filtrate, on addition of hydrochloric acid and application of heat, shows abundant indications of arsenic.

Minute traces of this metal may also be satisfactorily recognized by the magnesia-test, as is shown by the following experiments; 100 grains of electrotype-copper and 0·10 grain of arsenic acid were dissolved in nitric acid. Ammonia was added in excess, and subsequently a small quantity of solution of sulphate of magnesia. In a few hours, a distinct crystalline precipitate was observed upon the sides of the glass, which proved to be the arseniate of magnesia and ammonia. 0·02 grain of arsenic was added to 100·00 grains of copper, and treated in the same way. The liquid was allowed to remain for a few days, and the slight sediment, containing a basic salt of copper, was digested in sulphide of ammonium. Hydrochloric acid, added to the filtrate, caused a precipitate, which, on heating, assumed a pure yellow tint.

A method, published by one of us, in the Chemical Gazette for 1857 (vol. xv., p. 113), seems also to be advantageous in the quantitative estimation of arsenic and copper. Oxalic acid, added to a slightly acid solution of the two metals, precipitates nearly the whole of the copper, leaving the arsenic dissolved. The great practical difficulty, is the tendency which oxalate of copper possesses, of passing through filtering paper, even when double or treble filters are employed. This difficulty, however, may be overcome by adopting the following mode of operation. Ammonia is added to the solution of the metals in sufficient quantity to throw down the oxide of copper, without redissolving it. Oxalate of ammonia, poured in excess upon this precipitate, effects its solution, forming a double oxalate of copper and ammonia. The introduction of nitric acid causes a precipitate of oxalate of copper, which can be filtered with great readiness. Sulphide of ammonium, added in excess to the filtrate, throws down the small quantity of copper which has escaped precipitation by oxalic acid, at the same time holding the arsenic in solution, which may be estimated in the usual manner. The following experiments were instituted at the time of publication: —

A mixture of 50 grains copper and 0·5 arsenious acid = 0·378 arsenic, gave 0·365 grains of arsenic.

With a mixture of 40 grs. copper and 0·10 grain of arsenic, decided indications of the latter were obtained.

It appears, from the above results on the comparative merits of the three methods detailed for the detection of arsenic in copper, that the plan of precipitation by means of nitrate of lead exhibits very decided superiority over the other methods, not only in point of delicacy, but also as regards facility and rapidity of execution. Thus, less than 0·01 grain of arsenic in 100 grains of copper is readily discovered by means of the nitrate of lead-process within two hours, while, for the detection of more than double that proportion of arsenic by the method of Levol (*i. e.*, by its precipitate as the ammonio-magnesian salt), at least forty-eight hours must elapse before any conclusion can be arrived at.

When compared with the very delicate process of testing copper for traces of arsenic recommended by Dr. Odling, the nitrate of lead-method also offers considerable advantages, being quite equal to it in point of delicacy, and susceptible of far more rapid application. Dr. Odling suggests, that the finely divided copper to be tested should be exposed for a few days to the joint action of pure cold hydrochloric acid and of air. The resulting liquid, and any copper that remains undissolved are to be transferred to a retort and carefully distilled, the mouth of the retort dipping into water. Special tests for arsenic are then to be applied to the product of distillation. The addition of a small quantity of chlorate of potassa to the hydrochloric acid is recommended, to accelerate the solution of the copper, care being taken to keep the metal in excess, so as to ensure the complete decomposition of the chlorate before distillation. Dr. Taylor directs, that any copper remaining undissolved, after two or three days' exposure to hydrochloric acid and air, should be removed before distillation, its weight being deducted from that of the copper originally employed.

If, instead of allowing the copper to remain in prolonged contact with hydrochloric acid and air, at ordinary temperatures, it is introduced, together with a little hydrochloric acid, into a capacious vessel, and exposed to a gentle heat, the results of the experiment are considerably modified. A specimen of copper, containing only a very minute trace of arsenic, and in which that impurity had been distinctly detected, both by the

distillation-process, as just described, and by the nitrate of lead-method, was submitted to treatment with a small quantity of warm hydrochloric acid, in a Woulfe's bottle immersed in a water-bath. To this bottle were attached two others, the first containing water, into which the exit-tube of the heated bottle dipped, the second being partly filled with solution of acetate of lead. To the last bottle was attached a delivery-tube, which passed into a vessel containing a neutral solution of nitrate of silver. After continuing the application of heat for several hours, and examining the contents of the bottle containing water, in which any products of distillation had condensed, not a trace of arsenic could be detected, but in the nitrate of silver-solution was observed a very small black precipitate, resulting from the escape of hydride of arsenic from the apparatus. A similar experiment was made with a specimen of copper which contained about 0·3 per cent of arsenic. After exposure of this to heat, in contact with the acid, for a short time, it became coated with the grey film produced in applying Reinsch's test.* At the conclusion of the operation, which was continued for about four hours, no trace of arsenic was discovered in the condensed product, but an abundant precipitate was produced in the solution of silver. A specimen of copper, containing 1·1 per cent. of arsenic, was submitted to the same treatment for two successive periods of about two hours each. After both operations, the water in the condensing vessel contained only a very minute trace of arsenic, while the hydride of arsenic evolved was very considerable.†

It appears from these results that if, in exposing copper which contains arsenic to the action of hydrochloric acid, heat be applied,

* This grey deposit, which consists, according to Lippert (J. f. prakt. Chem. v. 81, p. 168), of an arsenide of copper having the composition Cu_3As, makes its appearance only slowly when a slightly arsenical copper is exposed to the joint action of hydrochloric acid and air. But if the acid be mixed with about half its volume of the ordinary test-solution of pure sesquichloride of iron, a grey film is very speedily produced, if the copper contain only a trace of arsenic, in consequence of the comparative rapidity with which the solution of the copper is then effected. For the same reason, the contact, for an instant, of a fragment of chlorate of potassa, with the copper immersed in hydrochloric acid, will produce a grey stain upon the metal, even if the proportion of arsenic present be very small indeed. It need scarcely be stated that, under ordinary circumstances, these tests are only useful as affording a preliminary indication of the extent to which a specimen of copper is contaminated with such metals as arsenic, antimony, lead, or bismuth.

† Sublimates of arsenious acid were obtained by heating a portion of the delivery-tube through which the gas passed from the lead- to the silver-solution. The experiments were expedited by passing a slow current of air through the apparatus.

the arsenic will continue for a considerable period to pass off only in the form of hydride of arsenic, even if it be present in the copper in very considerable proportion; and that it might, therefore, readily escape detection in the distillation process, if heat were at once applied, to aid in the solution of the copper, for the purpose of shortening the time required for the application of the test, as directed by Drs. Tay or and Odling. If the process of heating be continued for a long period, the disengagement of hydride of arsenic gradually diminishes, and eventually ceases almost entirely, as the amount of copper in solution becomes considerable, and as the fragments of metal become perfectly coated with the grey arsenide.

As a qualitative method of testing copper for arsenic and antimony, the plan of heating the metal with hydrochloric acid and carrying the evolved gas, purified as described, through nitrate of silver-solution, with the assistance of a slow current of air, can be recommended as comparatively very expeditious and exceedingly delicate; but, to identify each metal, when present in minute quantities, and to arrive at a knowledge of the proportion existing in the copper, by treatmen with hydrochloric acid, it is unquestionably necessary to effect the solution of the copper at ordinary temperatures, before distilling, and hence this method of examination is very tedious when compared with the process of separation by means of nitrate of lead and oxalic acid.

As regards the qualitative examination for *bismuth* in copper, considerable advantages, in point of delicacy and rapidity of execution over the quantitative method described in a former part of the paper, are possessed by a mode of testing for that metal, which is based upon a curious reaction exhibited by iodide of potassium in the joint presence of bismuth and lead, and which, we believe, has not hitherto been noticed. When iodide of potassium is added to a solution of a lead-salt, it is well known that yellow iodide of lead is precipitated, which dissolves on heating the liquid, and is re-precipitated, on cooling, in brilliant golden-coloured scales. (The solution of the amorphous iodide may be greatly facilitated by the addition of a small quantity of hydrochloric acid.) If the least trace of bismuth is present in the lead-salt, the re-precipitated scales are no longer yellow, but assume a dark orange or crimson tint, varying in intensity of colour according to the amount of bismuth present. This test is of such extraordinary delicacy, that 0·00025 of a grain of bismuth

may be detected in copper with the greatest ease, the iodide of lead becoming dark orange, while 0·001 grain imparts a reddish-brown tinge, and 0·01 grain a bright crimson, the scales resembling chromate of silver in appearance.

The mode of operation in applying this test is as follows:—About 100 grains of the copper to be examined are dissolved in nitric acid, a solution of nitrate of lead, equal to about 5 grains of the salt, is added, and subsequently ammonia and carbonate of ammonia. The precipitate is washed with ammoniacal water, to free it from copper, and dissolved in warm acetic acid. Considerable excess of iodide of potassium is introduced, and the liquid is warmed until the precipitate disappears. On cooling, the crystalline scales will shew, by their colour, the presence or absence of bismuth.* If in the same specimen of copper it is desired to test for arsenic and antimony, the nitrate of lead-precipitate is digested with oxalic acid. The oxalates of lead and bismuth are insoluble in acetic acid, and must therefore be dissolved in as small a quantity as possible of hydrochloric acid.

By the employment of the test just described, bismuth has been detected in many specimens of very pure copper. Nearly all the modern copper-coinage, more especially that of the reigns of George III. and IV., contains very considerable traces, and in the new bronze-currency it is abundantly evident. It is found also in the silver money of England, as well as of other countries, owing, probably, to the copper with which it is alloyed. Copper which has been rolled out to a ribbon, has been found to contain it to the extent of at least 0·02 per cent., while in some specimens of commercial sheet copper, as much as between 0·10 and 0·20 per cent. has been discovered. It may also be traced in nearly all copper gauzes, wires, and foil.

It might be presumed, from the nature of the methods described at the commencement of this paper, that bismuth would be separated from antimony and arsenic by means of oxalic acid. Numerous experiments have proved this to be the case. The precipitate occasioned by nitrate of lead, after digestion in oxalic acid,

* Iodide of lead is very soluble in the acetates of soda, potassa, and ammonia, even in the cold, forming colourless solutions, from which iodide of potassium, added in excess, precipitates iodide of lead in the crystalline state, although no heat has been applied. Gmelin, in mentioning many solvents of this compound, does not allude to the acetates of the alkalies, which dissolve it with infinitely greater ease than any of the others which are mentioned.

is entirely deprived of any antimony or arsenic with which it might have been previously associated, while the whole of the bismuth remains undissolved.

We append to this paper a tabular statement of the results obtained by an application of the methods of analysis, specially recommended in this paper, to the qualitative and quantitative examination of a large number of varieties of copper, which includes specimens of blister, bar, and refined copper from Chile, Mexico, Australia, North America, Buenos Ayres, Manilla, Spain, Russia, Sweden, Norway, Italy, and Hungary; numerous specimens of English "*best-select*" copper, of sheet and bolt-copper, and also several English and foreign coins.

The results of these examinations lead us to the following conclusions regarding the principal metals associated with copper:

1°. Arsenic and silver are almost invariable impurities in copper;

2°. The occurrence of bismuth in copper is very general; this metal seems to be absent only in those cases in which carbonates of copper have been alone employed in the production of the metal, as in the majority of Australian and Russian coppers;

3°. Antimony is not nearly so general an impurity of copper as has been supposed. There appears little doubt that, in analyses for practical purposes, the bismuth existing in copper has been mistaken for antimony, inasmuch as the rough qualitative method of testing, by the addition of a large quantity of water to the strong solution of copper in nitric acid, commonly employed, furnishes a white precipitate which has been regarded as an indication of antimony;

4°. Lead is of very rare occurrence in cake-copper, both unrefined and refined, as sent into the market; but appears to be an almost invariable constituent of copper which has been manufactured into sheet or rod.

It may be observed, in conclusion, that iron, which, like sulphur, exists, as might be supposed, in considerable proportions in what is technically termed bar copper, is almost perfectly removed by the refining process.

Results of the Examination for Metallic Impurities, of different varieties of Copper.

Description of Copper.	Silver.	Arsenic.	Antimony.	Bismuth.	Lead.	Tin.	Iron.
Bar and Blister Copper.							
Chile, No. 1 Bar	Silver was detected in all these specimens, but not determined.	traces	..	traces	..	..	0·62
„ 2 „		traces	..	..	..	..	0·71
„ 3 „		traces	..	traces	..	..	0.85
„ 4 „		0·10	..	traces	..	..	0·91
„ 5 „		traces	traces	traces	..	..	0·62
„ 6 „		traces	..	traces	..	..	0·46
„ 7 „		traces	..	traces	..	..	0·52
„ 8 „		traces	..	traces	..	..	0·67
„ 9 „		traces	..	traces	..	..	0·64
„ 10 „		traces	traces	traces	..	..	0·52
„ 11 „		traces	..	..	..	..	0·62
„ 12 „		0·62	traces	..	..	..	0·50
„ 13 „		0·04	traces	..	..	..	0·43
„ 14 „		0·07	0·50	traces	..	..	0·51
„ 15 „		..	..	..	..	..	0·84
„ 16 „		0·40	traces	traces	..	..	1·64
„ 17 „		0·45	..	..	..	..	1·52
„ 18 „		traces	..	..	..	..	0·70
„ 19 „		0·50	0·20	..	..	..	0·08
„ 20 „		..	..	..	..	..	1 20
„ 21 „		..	traces	traces	..	..	0·98
„ 22 „		..	traces	traces	..	..	1·00
„ 23 „		traces	..	traces	..	..	1·20
„ 24 „		traces	..	traces	..	..	1·04
„ 25 „		traces	..	traces	..	..	1·12
„ 26 „		traces	..	traces	..	..	1·02
„ 27 „		traces	..	traces	..	..	0·84
„ 28 „		0·03	traces	traces	..	..	1·10
„ 29 „		..	..	..	..	..	0·75
„ Blister Copper ..		0·10	traces	traces	..	..	0·32
Matzatlan Copper		traces	..	traces	..	..	1·32
New Mexican		..	..	..	..	..	0·42
Spanish, No. 1		3·31	0·70	..	..	..	traces
„ 2	..	2·49	..	trace	..	..	„
„ 3	..	2·15	..	0·04	trace	..	„
„ 4	..	1 18	..	..	trace	..	„
„ 5	..	1 20	..	trace	..	..	„
„ 6	Silver was detected in all these specimens, but the quantities were not determined.	0·90	..	..	..	..	„
„ 7		0·30	..	..	..	..	0·21
„ 8		0·25	..	traces	..	..	0 35
Swedish, No. 1		0·25	0·20	..	..	..	0·31
„ 2		..	traces	..	..	..	0 20
Manilla Slab		1·24	0·65	0·05	..	..	traces
Buenos Ayres Slab		0·31	0·17	0·10	..	..	traces
Australian (Sydney)		..	..	..	..	..	1·01
„ (Sydney)		..	..	..	..	..	0·76
Refined Coppers.							
Chile, (Societé Italienne) ..		..	..	..	..	..	0·01
Chile, No. 2		0·04	..	..	..	..	0·03
„ 3		0·03	..	..	..	..	..
Spanish		traces	..	..	..	..	0·06
„ No. 2		0·63	..	..	..	..	..
Italian, No. 1		..	..	trace	..	..	..
„ 2		..	..	..	..	..	trace
Tuscan Rosette		..	..	trace	..	..	trace

RESULTS of the Examination for Metallic Impurities, of different varieties of Copper.

Description of Copper.	Silver.	Arsenic.	Antimony.	Bismuth.	Lead.	Tin.	Iron.
Russian (C.C.N.D.)	Present but not determined.	0·11	..	minute traces	..	..	..
„ No. 2		..	..	..	..	..	0·30
Hungarian		0·36	0·22	traces	..	..	trace
„ Rosette		0·06	0·12	..	..	..	„
Australian (Burra Burra) ..		..	0·02	..	..	..	trace
„ (Kapunda) ..		..	0·01	..	..	..	trace
Lake Superior		0·07	0·01	..	..	..	trace
Norwegian (Alten)		trace	..	..	..	..	trace
North American		0·22	..	..	..	..	trace
„ No. 2 ..		0·06	..	..	..	..	trace
„ No. 3 ..		trace	..	..	..	..	trace
English Tile		traces	0·07	traces	0·02	..	trace
English Best Select, No. 1		0·03	0·03	..	0·05	..	trace
„ „ No. 2		0·02	0·04	..	0·04	..	trace
„ „ No. 3		0·02	0·01	..	0·05	..	trace
„ „ No. 4		0·03	0·04	..	0·04	..	trace
„ „ No. 5		0·02	0·12	0·02	0·05	..	trace
„ „ No. 6		0·04	0·15	0·05	0·05	..	trace
„ „ No. 7		0·03	0·14	0·02	0·04	..	trace
„ „ No. 8		trace	0·13	0·07	trace	..	trace
„ „ No. 9		trace	trace	trace	trace	..	trace
„ „ No. 10		0·03	0·14	0·05	0·05	..	trace
„ „ No. 11		0·07	0·31	trace	0·17	..	trace
„ „ No. 12		0·05	0·15	trace	0·12	..	trace
„ „ No. 13		0·05	0·12	trace	0·13	..	trace
„ „ No. 14		0·05	0·14	trace	0·12	..	trace
„ „ No. 15		0·06	0·10	..	0·12	..	trace
„ „ No. 16		0·02	0·04	0·02	trace	..	trace
„ „ No. 17		0·03	0·06	..	0·04	..	trace
SHEET AND BOLT COPPER.							
Sheet, No. 1		0·07	trace	trace	0·13	0·07	..	trace
„ No. 2		0·05	0·08	0·02	0·09	0·15	..	trace
„ No. 3		0·07	0·12	trace	0·06	0·08	..	trace
„ No. 4		0·02	0·14	..	0·04	0·05	..	trace
„ No. 5		0·05	0·09	..	0·13	0·25	..	trace
„ No. 6		0·06	0·10	0·01	0·18	0·18	..	trace
„ No. 7		0·03	0·10	trace	0·10	0·40	..	trace
„ No. 8		0·05	0·06	trace	trace	0·15	..	trace
„ No. 9		0·03	0·12	trace	0·05	0·38	..	..
Bolt, No. 1		trace	0·07	..	0·02	0·13	trace	trace
„ No. 2		trace	0·01	..	0·02	0·22	trace	trace
COINS.								
Copper Coin, George III. ..	All these specimens contained silver, the proportions were not determined.	0·12	trace	trace	..	..	trace
„ „ George IV. ..		0·09	trace	trace	..	trace	trace
„ „ William IV. ..		0·04	..	trace	..	trace	trace
New Bronze Coin		trace	..	trace	..	not estimated	trace
Spanish Coin, 1856		0·30	..	trace	..	trace	0·03
Chile Coin, 1858		trace	..	trace	..	trace	0·04
United States Coin, 1849 ..		trace	..	trace	..	trace	trace
Chinese Coin		trace	..	0·04	..	trace	0·12
Old Italian Coin		trace	..	..	..	trace	0·21
*Bactrian Coin (181 B.C.) ..		..	..	trace	..	..	trace
Dutch Coin		..	..	trace	..	0·17	..
Copper rolled into thin ribbon		..	..	0·03	..	..	..

* This coin was kindly given to us by Walter Hawkins, Esq., from his valuable collection.

XXIII.—*On the General Distribution of Bismuth in Copper Minerals.*

By Frederick Field, F.R.S.E.

From the paper I had the honour of submitting to the Society, in conjunction with Mr. Abel, upon the metallic impurities in commercial coppers, it will have been observed, that many of the samples analysed were found to contain bismuth.

This metal was particularly sought for, owing to an opinion that bismuth, even in minute quantities, exercises a decidedly injurious effect upon copper. As it was detected in coppers brought from many parts of the world, it occurred to us that it must necessarily be associated very widely indeed with copper minerals, and probably existed as frequently with the sulphides of that metal, as sulphide of silver is known to exist with the sulphide of lead. It was necessary, in order to determine this fact, to make a very extended investigation of the minerals of copper from various sources, and, as far as possible, to be acquainted with the locality, and even the name of the mine, from which the specimens, intended for analysis, were derived, and I have been fortunate enough to obtain samples from some of the leading mineral districts with which we are acquainted. The investigation embraces analyses of different varieties of copper ore from England, Scotland, Ireland, Wales, France, Spain, Turkey, Russia, Africa, and Australia; as well as Chile, Peru, Mexico, the United States, Canada, and Cuba. It is to be regretted that specimens from Germany and other countries were not received in time to admit of publication in this paper. The method pursued for the qualitative estimation of bismuth, is described in the preceding paper; and it is merely necessary to mention, that it depends upon the extraordinary influence exerted by a salt of bismuth, when precipitated together with a lead-salt by iodide of potassium, a minute trace of the former metal imparting a strong red tinge to the yellow iodide, which is seen to greater advantage, when the double salt is dissolved in very dilute hydro-

chloric acid, at the boiling temperature, and allowed to cool slowly. As, in the majority of copper ores, iron exists to a very great extent, and is necessarily precipitated by ammonia, together with the lead and bismuth, it is more convenient to dissolve the mineral to be examined, in nitro-hydrochloric acid, expel all traces of nitric acid by boiling, and after filtration, precipitate the copper and bismuth upon metallic iron. After digestion in nitric acid, the examination may be conducted as previously directed. As the list of nearly fifty examinations, appended to this memoir, only includes those minerals in which bismuth has been found, it may be as well to cite a few instances in which it could not be detected.

Bismuth is absent in all the oxides, carbonates, and metallic coppers of Chile. In the phosphates (*Liebethenite* and *Tagilite*), and in the silicates *Chrysocolla* and *Dioptase;* in the arsenides *Domeykite* and *Algodonite,* and in the highly sulphuretted mineral *Guayacanite* ($3Cu_2S.As\ S_5$). It could not be recognized in the malachites from Siberia, Russia, Australia, and the west coast of Africa, nor in a specimen of double sulphide of copper and iron (Cu_2S,Fe_2S_3) from Coquimbo. Many other specimens (free from sulphur) were examined, but no bismuth could be obtained.

The conclusions deducible from the above experiments must lead us to suppose, that bismuth is seldom or never found in copper minerals free from sulphur; but on the other hand, that it is nearly always found in conjunction with the sulphides. The two instances just related, in which it is absent, are exceptions to the constancy of its presence, and it may be concluded that it exists to as great an extent, and in about the same proportion with sulphide of copper, as sulphide of silver to sulphide of lead.

It may be mentioned, that Mr. John Abel detected bismuth as tersulphide in some copper minerals in Copiapo; a fact which is rather interesting, as it was the first instance in which bismuth was found associated with copper in that part of South America.

COPPER MINERALS in which Bismuth has been detected.

No.	Locality.	Name of the Mine.	Copper per cent.	Bismuth.
1	Chile (Coquimbo) ..	Pique	44·12	Bismuth.
2	„ „ ..	Chaleco	38·58	„
3	„ „ ..	San José	42·64	„
4	„ „ ..	Tortolas	12·20	„
5	„ „ ..	Mollaccas	56·25	„
6	„ (Huasco) ..	Rosario	14·60	„
7	„ „	Bronce	16·81	„
8	„ (Coquimbo) ..	Rosario	11·20	„
9	„ „ ..	Menillas	18·40	„
10	„ (Copiapo) ..	Checo	21·20	„
11	„ „ ..	Cerro Negro	24·62	„
12	„ (Copiapo) ..	Tres Puntas	21·40	„
13	„ „ ..	Unknown	19·70	„
14	Peru (Tacna)	„	21·20	„
15	„ (Tacna)	„	14·10	„
16	„ (Tacna)	„	36·28	„
17	Mexico (Zacatecas) ..	„	11·20	„
18	„ (Somelhuacan)	„	21·00	„
19	„ (unknown) ..	„	2·80	„
20	„	San Salvador	37·70	„
21	Cuba	Unknown	14·40	„
22	„	„	23·50	„
23	„	„	12·50	„*
24	„	Cobre	22·40	„*
25	Canada West	Lake Huron	22·50	„*
26	North Carolina	Unknown	19·40	„
27	Ireland	Beachaven	12·60	„*
28	Wales (Anglesea) ..	Parry's Mine	21·60	„*
29	England (Cornwall) ..	East Caradou	9·90	„
30	„ „ ..	West Caradou	23·00	„
31	„ „ ..	South Caradou	9·90	„
32	„ „ ..	Great Wheal Martha	4·70	„
33	„ „ ..	Phœnix Mines	15·30	„
34	„ „ ..	Devon and Cornwall United.	3·70	„
35	„ „ ..	Great Wheal Busy	5·40	„
36	„ „ ..	Fowey Consols	6·90	„
37	„ „ ..	United Mines	5·20	„
38	„ „ ..	Treleigh Consols	5·80	„
39	„ „ ..	Craddock Moor	9·80	„
40	„ „ ..	Pembroke	7·10	„
41	„ „ ..	North Wheal Busy	11·90	„
42	„ (Devonshire)	Devon Great Consols	5·00	„
43	France	Unknown	7·20	„
44	Spain	Garrucha	17·60	„
45	„	Del Soto	17·40	„
46	„	Unknown	9·40	„
47	Turkey	„	13·20	„
48	Africa	Ookip	36·90	„
49	Australia	Wheal Maria	27·70	„

* These specimens had very minute traces.

XXIV.—*On Leucic Acid and some of its Salts.*

By J. Louis W. Thudichum, M.D.

Preparation.—When pure leucine is dissolved in warm water and treated with nitrous acid gas, it is decomposed, with evolution of nitrogen. The liquid froths very much, and assumes a reddish colour. When the reaction ceases, which is generally the case after three or four hours, the fluid is evaporated to a small bulk or syrupy consistence on the water-bath, and allowed to cool. If, as should be the case, a quantity of undecomposed leucine is present, the fluid shoots into a crystallised mass of nitrate of leucine surrounded by a syrupy acid. This mixture is transferred to a stoppered bottle, and treated with repeated quantities of ether, which dissolves leucic acid, leaving nitrate of leucine in splendid crystals undissolved. Crystals and solution are separated by the filter, the ether is distilled off the filtrate, and the syrupy residue, of a slightly yellowish colour, is evaporated on the water-bath for a short time. It is next dried over sulphuric acid, when overnight crystallisation begins from the margin of the syrup, which, in the course of a few days, involves the whole liquid.

From the watery solution in which it was found, leucic acid may be extracted by ether directly, without the assistance of preliminary evaporation. In this case, the solution must be treated with repeated quantities of ether, otherwise much leucic acid remains in solution. When evaporation is had recourse to, it is best to add a little leucine to the fluid, which combines with the free nitric acid, and prevents it from exerting any oxydizing influence upon the leucic acid.

Properties.—The crystals are needles placed in radiary arrangement, the centres being at the periphery of the surface of the liquid where it touches the dish. The crystallised masses have the lustre of mother-of-pearl, with a beautiful variety of concentric markings, resembling the markings of some descriptions of larch-agarics, in a much higher degree than the clusters of leucine itself, which have been so described.

Impure and dark-coloured leucic acid crystallises much more

slowly than the pure acid. It requires about a week of standing over sulphuric acid, before a start is effected, and even then the formation of crystals proceeds but slowly.

Purification.—The acid thus obtained may be purified after crystallisation by re-solution in cold water and filtration. An insoluble dark-brown oily matter remains on the filter. The crystallised acid may also be pressed between folds of bibulous paper; but unless a good press or a vice be employed, much liquid will not be removed thereby. On the whole, the purification of leucic acid is a difficult and tedious process. The greatest care should therefore be taken to employ pure leucine for the production of the acid. Nevertheless, the apparently purest leucine not unfrequently yields a yellow solution. This is best treated with acetate of lead, which precipitates leucate of lead in white copious flakes, to be dissolved in boiling alcohol after washing with water; the precipitate, after washing with cold alcohol, and suspension in water, is to be decomposed by hydrosulphuric acid. The watery solution should be evaporated on the water-bath at a very low temperature or over sulphuric acid.

Chemical Properties.—Leucic acid cuts under the knife like hard soap, almost like stearic acid, and is very soluble in water. A small piece, placed in water, is rapidly dissolved, producing curious currents of diffusion. This phenomenon is most remarkable when watched with the aid of the microscope.

Leucic acid is heavier than water. Its solution has an agreeably acid taste, reddens litmus, and decomposes carbonates, the acid combining with their bases.

It is soluble in alcohol and ether.

When heated below the boiling point of water, it fuses, and, on cooling, solidifies again. When the heating in the water-oven is continued for several hours, the evolution of acid-smelling vapours is continually perceived. On cooling, the acid does not, however, again solidify; it becomes more consistent, but remains an uncrystallisable, dark-brown, smeary syrup, which, after standing for weeks over sulphuric acid, undergoes no change, and is found to be nearly insoluble in water, separating from it like oil, and sinking to the bottom. It emits a very disagreeable odour. When leucic acid, even in dilute solutions, is heated to the boiling point, or when its solution is evaporated, a small quantity of this insoluble compound is always formed. It is the admixture of this substance which makes the production of pure salts of leucic acid a matter

of some difficulty. This peculiar change also explains the statement which I have seen put forth in Schlosser's "Handbuch der Chemie," that leucic acid is not crystallisable. It is highly crystallisable, but easily becomes transformed into an uncrystallisable body, by exposure to a temperature not exceeding the boiling point of water. The properties of the new substance I have not studied any further.

When heated strongly, leucic acid gives out thick fumes, and blackens, then takes fire and burns with a fuliginous dark-yellow flame, leaving a small quantity of charcoal, which is quickly and easily consumed.

Composition and Analyses.—I. 6·447 grains of crystallised acid, dried over sulphuric acid, and burnt from a platinum boat in a current of oxygen, yielded 12·703 grains of carbonic acid and 5·047 grains of water, corresponding to 53·73% of carbon and 8·68% of hydrogen.

II. 5·473 grains yielded 10·792 grains of carbonic acid and 4·337 grains of water, corresponding to 53·77% of carbon and 8·80% of hydrogen.

III. 5·645 grains yielded 11·220 grains CO_2 and 4·402 HO, equal to 54·20% C, and 8·66% H.

			Found.		
	Equivalents.	In 100 parts.	I.	II.	III.
C_{12}	72	54·54	53·73	53·77	54·20
H_{12}	12	9·09	8·68	8·80	8·66
O_6	48	36·37	,,	,,	,,
	132	100·00			

Taking into consideration the known formula of leucine, $C_{12}H_{13}NO_4$, and the equivalent of leucic acid, as ascertained by the analyses of some of its salts stated below, the above figures lead to the formula $C_{12}H_{12}O_6$.

Both carbon and hydrogen were found too low in the analyses, while the same acid furnished salts, which, like that of cobalt, yielded the most accurate figures on analysis. On re-solution of another portion of the acid, used for combustion, it was found that a small portion had again been transformed into the dark, oily body insoluble in water.

The mode of burning leucic acid in the platinum boat, in a current of oxygen, is not the most suitable, as in case the acid is

heated a little too rapidly, explosions are likely to ensue within the combustion-tube, which easily disarrange the apparatus and cause the loss of the analysis.

Leucate of Ammonia.—Leucic acid neutralised with ammonia in slight excess, and evaporated, leaves a thick homogeneous residue, in which no crystallisation can be observed, even after it has been drying over sulphuric acid for several weeks.

Leucate of Soda.—A watery solution of leucic acid, carefully saturated with carbonate of soda and evaporated, leaves a syrupy residue covered with a crystalline crust. On standing over sulphuric acid, crystals form in the syrup, which, under the microscope, have a characteristic tub-shape, with rhombic plates interspersed here and there. The crystals could not be sufficiently isolated and purified for analysis.

Leucate of Lime.—$C_{12}H_{11}CaO_6$. A dilute solution of leucic acid, while boiling, is neutralized with carbonate of lime. The filtrate, on evaporation, yields crusts of a salt which I have not been able to observe in a crystalline state. The salt cannot be purified by recrystallisation, and retains the yellow colour which it assumed during boiling.

I. 0·776 grm., dried at 100° C., yielded 0·337 grm. of sulphate of lime, corresponding to 12·78% of calcium.

II. 0·588 grm. gave 0·2535 grm. of sulphate, corresponding to 12·68% Ca.

	I.	II.	Calculated.
Ca	12·78	12·68	13·24

Leucate of Magnesia.—A very dilute solution of leucic acid is neutralized with carbonate of magnesia. The salt is very little soluble in water, and, like the zinc-salt, is deposited in crusts on evaporation.

Leucate of Baryta.—A dilute watery solution of the acid is neutralized with the carbonate while boiling. After filtration and evaporation, crystalline crusts of the salt are obtained. Pressed between bibulous paper and dried, the salt retains a yellow colour.

Leucate of Cobalt.—A dilute aqueous solution of leucic acid is boiled with an excess of carbonate of cobalt. The rose-coloured filtrate, on evaporation, deposits light crusts of a pink colour while moist, but of a very pale rose colour, or almost white when dry. This salt is not much more soluble in boiling than in cold water. Its solubility in this menstruum is, on the whole, limited.

It crystallises in needles, which, when seen under the microscope, appear arranged in globular masses. To the naked eye these globules appear as little warts imbedded in crusts showing no structure.

Analyses and Composition.—I. 7·9 grains, on combustion, left 24·55%; viz., 1·94 grains of residue, being Co_3O_4, of which, theoretically, 25·25% should be left. After treatment with nitric acid and exposure to heat, the percentage value of the residue rose to 26·49%, but fell again to 23·54% after prolonged exposure to a light red heat. After reduction with hydrogen, there were left 1·46 grains of metallic cobalt, corresponding to 18·48%.

II. 2·570 grains, on combustion, left 0·62 grains, or 24·12% Co_3O_4; and, on treatment with hydrogen, left 0·470 grains Co, equal to 18·28%.

These figures again show that no constant compound of oxygen and cobalt can be obtained by exposure of a salt to heat, and that cobalt must be quantitatively determined in its metallic state.

The average of the two determinations exactly corresponds with the theoretical amount; viz., 18·38%.

III. 0·4615 grm., on combustion with oxyde of copper, yielded 0·7611 grm. of carbonic acid and 0·2802 of water, corresponding to 44·97 per cent. of carbon and 6·75% of hydrogen.

IV. 0·280 grm. yielded 0·4586 grm. CO_2 and 0·1712 grm. HO, corresponding to 44·67 C, and 6·79% H.

			Found.			
	Equiv.	In 100 parts.	I.	II.	III.	IV.
C_{12}	72	44·85	,,	,,	44·97	44·67
H_{11}	11	6·85	,,	,,	6·75	6·79
Co	30	18·38	18·48	18·28	,,	,,
O_6	48	,,				
	161					

Leucate of Zinc.—Dilute leucic acid, while boiling, is treated with carbonate of zinc. The salt in solution is filtered while boiling hot. If the solution of leucic acid was not exceedingly dilute, a thick froth, containing undissolved salt and carbonate, is formed at the top of the liquid, which requires repeated boiling with water before it is dissolved. The latest solutions are the purest and least coloured. The solution of the leucate deposits a thin

crust on cooling. On evaporation over the water-bath, it soon becomes covered with a crust, and on cooling, deposits voluminous masses of needles. They are separated by the filter, pressed between bibulous paper, and dried by exposure to air, or over the water-bath.

The salt is white, like snow, and of a splendid silky lustre. Under the microscope, masses of needles are observed, which, in the crusts, are seen to form dark globular masses. It is little soluble, even in boiling water; less soluble in cold. At 100°C., the salt parts with little more than half the moisture which it retains when air-dry. It requires a temperature between 120° and 130°C. to dry it completely.

Hydrosulphuric acid precipitates only a portion of the zinc from a solution of the salt. Even after repeated saturation of dilute and concentrated solutions with this gas, such an amount of zinc remains in the liquid, that, on concentration and cooling of the solution, the zinc-salt crystallizes in splendid needles. The best mode of producing the zinc-salt in a pure and crystallised state, is to let it crystallise from an excess of leucic acid.

Analyses and Composition.—

			Found.				
	Equiv.	In 100 parts.	I.	II.	III.	IV.	V.
C_{12}	72·0	44·01	43·83	43·95	43·84	,,	,,
H_{11}	11·0	6·72	6·79	7·08	6·82	,,	,,
O_5	40·0	24·45	,,	,,	,,	,,	,,
ZnO	40·6	24·82	,,	,,	,,	25·45	24·65
	163·6	100·00					

I. 0·4243 grm. of salt, on combustion with oxide of copper, gave 0·6820 grm. of carbonic acid and 0·2596 grm. of water, corresponding to 43·83% C and 6·79% H.

II. 0·2850 grm. of substance yielded 0·4593 grm. CO_2 and 0·1817 grm. HO, corresponding to 43·95% C and 7·08% H.

III. 0·320 grm. of salt gave out 0·5143 grm. CO_2 and 0·1965 grm. HO, equal to 43·84% C and 6·82% H.

IV. 0·4380 grm. of salt, dissolved in hydrochloric acid, precipitated with carbonate of potassa, after exposure to red heat, left 0·1115 grm., corresponding to 25·45% ZnO.

V. 7·923 grains of salt, dissolved in hydrochloric acid, and precipitated by carbonate of soda while boiling, yielded 1·958 grain, or 24·65% of ZnO.

Leucate of Suboxide of Mercury.—When to a solution of leucic acid a solution of nitrate of suboxide of mercury is added, a slight turbidity ensues. The addition of carbonate of soda produces a copious reddish-white precipitate, which, on boiling, becomes red, then dull grey, and deposits metallic mercury at the bottom of the tube.

Leucate of Oxide of Mercury may be prepared,—

a. Directly, by dissolving freshly precipitated moist oxide of mercury in an aqueous solution of leucic acid. A flaky precipitate gradually ensues, which, on heating, becomes red and granular, and adheres to the sides of the glass. On cooling, a new precipitate, consisting of whitish globules, is deposited.

b. By adding nitrate of protoxide of mercury to an aqueous solution of leucic acid. A whitish-red precipitate is then formed, which dissolves on boiling, and, on cooling, is again deposited in reddish granules.

c. By adding the mercurial solution to the leucate of an alkali.

The leucates of both oxides of mercury have a great tendency to become reduced. The salt of the oxide easily passes into that of the suboxyde. The salt of the oxide, moreover, has a great tendency to become basic and insoluble. For these reasons, the salts have not been analysed.

Leucate of Copper.—When a dilute aqueous solution of leucic acid is treated with a dilute solution of ammonio-sulphate of copper, the colour of the copper-salt changes to light green. On boiling the liquid, it becomes paler, and, on cooling, deposits light green granules of leucate of copper. Under high powers of the microscope, these granules appear as balls, formed by a radiary arrangement of needles. The smallest balls are more suitable for seeing this arrangement than the larger ones, which are not sufficiently transparent.

The salt is very little soluble in cold,—more soluble in boiling water. Dried at 130°, it left, on combustion in the platinum crucible and treatment of the residue with nitric acid and renewed exposure to heat, a quantity of oxide which corresponded to 23·26%.

	Equivalents.	In 100 parts.	Found.
C_{12}	72	,,	,,
H_{11}	11	,,	,,
O_5	40	,,	,,
CuO	39·68	24·3	23·26
	162·68		

Leucate of Silver.—A hot dilute solution of leucic acid decomposes recently prepared carbonate of silver with effervescence. The excess of the silver and the undissolved portion of the leucate become blackish-grey, but the acid is not entirely neutralized. The hot filtrate forms no deposit on cooling. The attempt to evaporate it over the water-bath produces a black precipitate of reduced silver. It must, therefore, be evaporated under the air-pump with the aid of sulphuric acid. After prolonged standing, a few crystals, of a glassy lustre and appearing under the microscope as groups of rhombic plates, are deposited at the margin of the dish. The liquid then becomes covered with a pellicle, and evaporation is impeded. At a later stage, conglomerates of needles are deposited, which, when carefully dried over sulphuric acid in vacuo, appeared a little blackened, like most silver-salts, but not decomposed. 0·4606 grm. yielded 0·1242 grm. of silver, equal to 26·97 per cent. The bileucate of silver $(C_{12}H_{11}AgO_6)+C_{12}H_{12}O_6$, requires 29·1% of silver.

By adding nitrate of silver to a warm solution of leucate of potassa, or soda, or ammonia, a copious, white, amorphous precipitate is produced, which increases as the liquid cools. It soon blackens when allowed to stand in the mother-liquor. Filtered, washed, and dried over sulphuric acid, it yielded by analysis the following result:—

2·186 grains left, on combustion, 0·965 grain of silver, or 44·14%.

	Equivalents.	In 100 parts.	Found.
C_{12}	72	,,	,,
H_{11}	11	,,	,,
Ag	107·97	45·18	44·14
O_6	48	,,	,,
	238·97		

On drying over the water-bath below 100°, this salt became brown,

and continued to lose weight. After many useless attempts, I abandoned its further analysis.

Leucate of Lead.—On adding acetate of lead to a solution of leucic acid, or a suitable leucate, a copious white precipitate is produced, which is flaky, and, on boiling, almost entirely dissolves in the fluid. Any portion remaining undissolved melts into a white mass, which is soft like resin while warm, but becomes brittle and hard on cooling. This substance is insoluble in water and alcohol, even on boiling, and seems to be a basic salt.

If the solution of lead is added to a boiling solution of the acid, no precipitate ensues, acid vapours are evolved, and the liquid becomes milky on cooling. In a short time, it deposits the new salt as a light, granular, white mass, which, under the microscope, appears to be made up of a multitude of spherical masses, which strongly refract light, and are of the size of human blood-corpuscles.

This salt is more easily soluble in an excess of the acetate than in water. It is easily soluble in spirit of wine, particularly in boiling spirit. Even in these solutions basic salts are easily formed. The addition of water to these solutions produces a precipitate.

The bibasic salts of lead and mercury, and the peculiar—perhaps acid—silver-salt, are subjects for further enquiry. The attempt to produce an acid baryta-salt, by evaporating two equal quantities of acid, one of which had been neutralized with carbonate, produced a mixture of neutral salt and leucic acid, having the form of a smeary, half-solid mass. That the neutral zinc-salt crystallizes from acid solutions, I have already stated.

The foregoing paper is the commencement of an enquiry into the nature and transformations of those amido-acids which play a part in the normal or abnormal chemical processes in man and animals.

Contributions to the History of the Phosphorus Bases.

By Augustus William Hofmann, F.R.S.

[Abstracted from a series of papers read before the Royal Society, June 21, 1860.]

THIRD MEMOIR.

Phosphammonium and Phospharsonium-, Diarsonium- and Arsammonium-Compounds.

In the former section of this inquiry, I have endeavoured to trace the history of the bodies which are generated by the mutual action of triethylphosphine and dibromide of ethylene. Endeavouring, as far as possible, to fix with precision the several phases of this reaction, I have also carefully studied its principal products, the history of which appears to open the clearest perception of the nature of the polyatomic ammonias, and more especially of their connexion with the monatomic bases. The four saline compounds which, in accordance with the indications of theory, are formed by the action of dibromide of ethylene upon triethylphosphine, the bromides of the bromethylated, oxethylated, and vinylated monophosphonium, and of ethylene-diphosphonium, represent, in the phosphorus-series, as well as in the nitrogen and arsenic series, four classes of salts, the individual terms of which admit of being constructed in unlimited number and endless variety.

The following pages are devoted to the consideration of several compounds belonging to these four principal groups. The examination of the mixed diatomic bases of the phosphorus-nitrogen, phosphorus-arsenic- and arsenic-nitrogen-series, have more especially engaged my attention. Before, however, proceeding to a detailed account of these substances, which form more particularly the subject of this paper, a few experiments may still be briefly mentioned which are even more closely connected with the observations recorded in the previous memoir.

Action of Dichloride of Ethylene on Triethylphosphine.

It is precisely analogous to that of dibromide of ethylene, giving rise to the two compounds—

$$C_8H_{19}P\,Cl_2 = [(C_2H_4Cl)\ (C_2H_5)_3P]Cl, \text{ and}$$

$$C_{14}H_{34}P_2Cl_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' Cl_2.$$

If the reaction be suffered to go on to the end under the influence of heat, the resulting white crystalline mass consists

almost entirely of the diphosphonium-compound, no matter in what proportions the two bodies may be mixed, or whether they act upon one another in absence or in presence of alcohol or ether. To obtain the monatomic compound, a mixture of triethylphosphine with a very large excess of chloride of ethylene must be left to itself for some days. The white crystalline needles which the liquid deposits, are mixed even then with a considerable quantity of the diphosphonium-compound; but on treating their solution with dichloride of platinum, and leaving the pale-yellow precipitate, which exhibits an unmistakeable diphosphonic character, at rest for some hours, it becomes traversed by a number of deep orange-yellow crystalline stars, which may easily be separated from the yellow powder by mechanical rinsing. By boiling the yellow powder with water, an additional quantity of this orange-yellow salt is obtained, which may be purified, together with the first portion, by recrystallization. This salt resembles in most respects the platinum-salt of bromethylated triethylphosphonium; it is, however, somewhat more soluble, and exhibits a more decided tendency to assume the octohedral character. The properties of this body plainly show that it is the *platinum-salt of chlorethylated triethylphosphonium:*

$$C_8H_{19}P\,Pt\,Cl_4 = [(C_2H_4Cl)(C_2H_5)_3P]Cl,\,Pt\,Cl_2.$$

The chloride prepared from the needle-shaped platinum-salt by sulphuretted hydrogen yielded, when treated with oxide of silver, a caustic liquid, which, after addition of hydrochloric acid and dichloride of platinum, deposited the well-known octohedra of the oxethylated phosphonium-salt:

$$[(C_2H_5O)(C_2H_5)_3P]Cl,\,Pt\,Cl_2.$$

No doubt could exist respecting the nature of the sparingly soluble diphosphonium-platinum-salt.

The formula

$$C_{14}H_{34}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\,2\,Pt\,Cl_2$$

was, nevertheless, established by experiment.

The compounds of chlorethylated triethylphosphonium are likewise formed under conditions similar to those which have already been mentioned as leading to the reproduction of the bromethylated from the oxethylated salt. On subjecting the chloride of oxethylated triethylphosphonium to the influence of pentachloride of phosphorus, a violent reaction takes place, attended with evolution of vapours of oxychloride of phosphorus. If the chloride of phosphorus be added by small portions till no further action is perceptible, and the mixture be then digested till the

hydrochloric acid, the oxychloride, and any excess of pentachloride are driven off, the chloride of the chlorethylated compound remains in the retort.

$$[(C_2H_5O)(C_2H_5)_3P]Cl + PCl_5 = POCl_3 + [(C_2H_4Cl)(C_2H_5)_3P]Cl + HCl.$$

To fix the nature of this reaction by a number, the solution of the residual chloride was precipitated with dichloride of platinum. On recrystallizing the platinum-precipitate from boiling water, the beautiful needles characteristic of the chlorethylated compound immediately made their appearance, which on analysis were found to contain,

$$[(C_2H_4Cl)(C_2H_5)_3P]Cl, PtCl_2$$

Monochlorinated chloride of ethyl acts on triethylphosphine like dichloride of ethylene. At the common temperature, and with a large excess of the chlorinated compound, the chloride of chlorethyl-triethylphosphonium is produced, which was easily identified by the reaction with excess of nitrate of silver and ammonia, repeatedly mentioned in the previous memoir. At the temperature of 100°, and with a considerable excess of triethylphosphine, crystals of the dichloride of ethylene-diphosphonium are soon deposited. The nature of the latter was fixed by the preparation of the characteristic platinum-salt, and of the beautifully crystallized di-iodide.

Action of Di-iodide of Ethylene on Triethylphosphine.

The two bodies, in the absence of solvents, act upon one another with explosive violence. The heat evolved causes the iodide of ethylene to resolve itself into ethylene and iodine, which unites directly with the phosphorus-base. If the violence of the action be diminished by admixture of alcohol, a white crystalline mass is obtained consisting almost entirely of the hydriodate of the phosphorus-base.

If the compounds

$$[(C_2H_4I)(C_2H_5)_3P]I \text{ and}$$

$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2$$

are likewise formed, they must be present in extremely small quantities only. The crystals, dissolved in water and decomposed by baryta, left, after the triethylphosphine had been removed by ether, the iodine by oxide of silver, and the baryta by means of carbonic acid, scarcely traces of an organic compound. The triethylphosphine evidently acts upon iodide of ethylene just like

an alcoholic solution of potassa, the chief phase of the reaction doubtless consisting in the transformation:

$$(C_2H_5)_3P + (C_2H_4)I_2 = [(C_2H_5)_3HP]I + C_2H_3I.$$

I should not omit to mention, however, that the production of iodide of vinyl (C_2H_3I) was not demonstrated by a special experiment. There was some probability of an iodethylated triethylphosphonium-compound being formed by the action of iodide of phosphorus on the chloride or iodide of the oxethylated metal; but these bodies do not act on one another.

Hybrids of Ethylene-Diphosphonium.

In a former paragraph, I mentioned as a fact of peculiar interest, the formation of the dibromide of hexethylated ethylene-diphosphonium by the reaction

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3P = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$$

The study of this reaction naturally led me to try that of trimethylphosphine on the bromide of bromethylated triethylphosphonium, which I had a right to expect would thus be converted into the dibromide of ethylene-trimethyl-triethyldiphosphonium:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (CH_3)_3P = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$$

Action of Trimethylphosphine on Bromide of Bromethyl-triethylphosphonium.

These two bodies act upon each other with the greatest energy, and moreover exactly in the manner indicated by theory. The resulting compound was, of course, examined only as far as necessary to establish the character of the reaction. The bromide of the hybrid diphosphonium is more soluble than the similar diphosphonium-compound previously described, which in other respects it greatly resembles. Oxide of silver eliminates the extremely caustic base,

$$C_{11}H_{30}P_2O_2 = \left[(C_2H_4)''(CH_3)_3(C_2H_5)_3P_2\right]''\begin{matrix}\\H_2\end{matrix}\Big\}O_2,$$

which yields with hydrochloric acid and dichloride of platinum, a pale-yellow platinum-salt,

$$C_{11}H_{28}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2, 2PtCl_2,$$

crystallizing in scales from boiling water.

The salts of the hybrid diphosphonium crystallize like those of the corresponding hexethylated compound, but, as far as they have been examined, are somewhat more soluble; this remark applies especially to the di-iodide.

It seemed worth while to try whether the bromide of bromethylated triethylphosphonium was capable of fixing a molecule of *phosphoretted hydrogen*. I found, however, that the two bodies do not act upon one another. Phosphoretted hydrogen gas, passed through the alcoholic solution of the bromide, either cold or boiling, did not seem to affect it in any way.

Action of Dibromide of Ethylene on Trimethylphosphine.

This reaction exhibits a repetition of all the phenomena observed in that which takes place between the dibromide and triethylphosphine. The process is completed, if possible, even sooner than in the ethyl-series. The lower boiling-point and overpowering odour of the trimethylphosphine render it advisable to mix the materials with considerable quantities of alcohol or ether; moreover, on account of the extreme oxidability of the phosphorus-compound, it is necessary to operate in vessels filled with carbonic acid and immediately sealed before the blowpipe. After digestion for a short time at 100°, the mixture of the two liquids solidifies to a hard, dazzling white, crystalline mass, containing the two bromides,

$$C_5H_{13}PBr_2 = [(C_2H_4Br)(CH_3)_3P]Br, \text{ and}$$

$$C_8H_{22}P_2Br_2 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(CH_3)_3P\end{matrix}\right]''Br_2,$$

one or the other predominating, according to the proportions in which the two bodies were allowed to act upon one another.

It is not difficult to establish by numbers the formation of these two bodies.

Bromide of Bromethyl-trimethylphosphonium.—When a solution of trimethylphosphine in absolute alcohol, mixed with a very large excess of dibromide of ethylene, is exposed for some hours to a temperature of from 50° to 60°, the liquid on cooling deposits well-formed crystals. It is desirable not to pass this temperature; at the boiling point of water the mixture turns brown, in consequence of secondary reactions. One or two crystallizations from absolute alcohol render the crystals perfectly pure; they exhibit in this state the chemical and physical characters of the corresponding ethylated body, possessing, however, a different crystalline form.

The formula is

$$C_5H_{13}PBr_2 = [(C_2H_4Br)(CH_3)_3P]Br.$$

Platinum-salt.—This is easily formed by treating the bromide with chloride of silver, when a crystallizable chloride is produced, which yields with dichloride of platinum splendid orange-yellow needles, containing

$$C_5H_{13}PBrPtCl_3 = [(C_2H_4Br)(CH_3)_3P],PtCl_2.$$

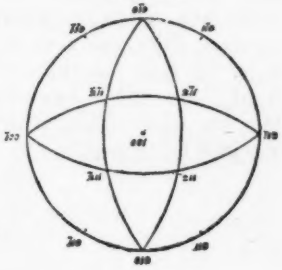
I have already mentioned that the bromide of bromethyl-trimethylphosphonium crystallizes differently from the bromide of the ethylated body. Whilst the latter is obtained in rhombic dodecahedrons, the methylated bromide affects forms belonging to the trimetric system. Quintino Sella has made the following examination of this compound:—

"System trimetric:—

100, 110 = 60° 24′;

001, 101 = 22° 9′.

Fig. 54.*



Forms observed:—

100, 010, 001, 110, 211 (Fig. 54).

Combinations observed:—

100, 010, 001; 110 (Fig. 55).
100, 010, 001; 110, 211 (Fig. 56).
110, 001; 100 (Fig. 57).
110, 001; 100, 010, 211 (Fig. 58).
001, 010, 211 (Fig. 59).

Fig. 55.

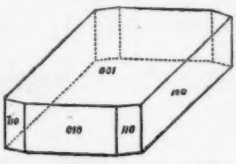
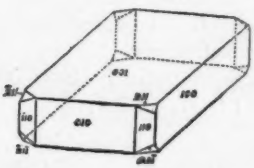


Fig. 56.



* The figures are numbered consecutively with those in Dr. Hofmann's former paper on the Phosphorus Bases, Vol. XIV, p. 73.

Fig. 57.

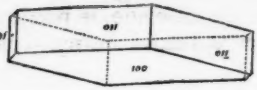


Fig. 58.

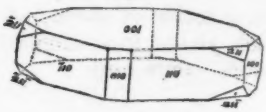
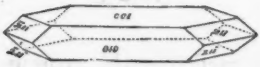


Fig. 59.



The crystals are generally tabular, as in the above figures; sometimes, however, they are elongated in the direction [0 0 1], and then the faces are most unequally developed. Figs. 60 and 61, and, again, Figs. 62 and 63 exhibit two very remarkable crystals of this kind.

The faces of the form 2 1 1 are generally very unequally developed, and some are actually wanting. In the crystals Figs. 60 and 61, and, again, Figs. 62 and 63, only two out of the eight faces 2 1 1 were well developed. The six others were wanting, or could but just be traced.

Fig. 60.

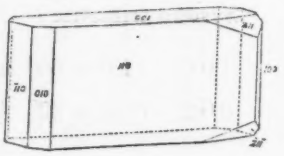


Fig. 61.

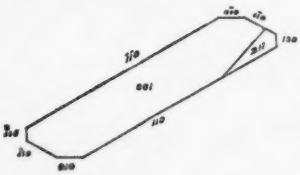


Fig. 62.

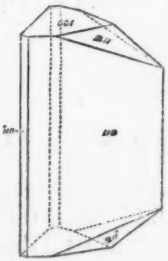
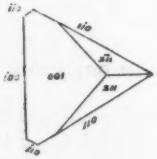


Fig. 63.



The lustre of the faces 0 0 1 is glassy, or even pearly. The lustre of the other faces is less marked, and more fatty.

Cleavages 0 0 1 easily obtained and rather perfect; 1 1 0 easily obtained, but fibrous.

The axes of optical elasticity, in the order of magnitude, are [0 0 1], [1 0 0], [0 1 0]."

Compounds of Oxethyl-trimethylphosphonium.

The liquid filtered from the sulphide of platinum, in the analyses of the platinum-salt of bromethyl-trimethylphosphonium, yielded by evaporation the extremely soluble and deliquescent

chloride. This salt has not been analysed; but I have transformed it, by oxide of silver, into the corresponding oxethylated compound,

$$C_5H_{15}PO_2 = \left.\begin{matrix}[(C_2H_5O)\ (CH_3)_3P] \\ H\end{matrix}\right\} O.$$

The caustic liquid is converted by hydrochloric acid into the easily soluble chloride corresponding to the hydrate; this chloride, treated with dichloride of platinum, yields the platinum-salt of oxethylated trimethylphosphonium, which crystallizes in octohedra, like the corresponding ethyl-compound, but is distinguished from the latter by its extraordinary solubility in water. It was found to contain:

$$C_5H_{14}PO\,PtCl_3 = [(C_2H_5O)(CH_3)_3P]Cl,\,PtCl_2.$$

Salts of Ethylene-hexmethyl-diphosphonium.

Dibromide.—This salt is formed when dibromide of ethylene is treated with an excess of trimethylphosphine. The reaction is rapidly accomplished at the temperature of boiling water. The salt resembles the dibromide of the ethyl-series in its properties. It is extremely soluble, and was only once obtained in well-defined crystals, which were analysed and determined. Many efforts were made to produce these well-formed crystals a second time, but without success. Formula:

$$C_8H_{22}P_2Br_2 = \left[(C_2H_4)'' \begin{matrix}(CH_3)_3P \\ (CH_3)_3P\end{matrix}\right]'' Br_2,$$

The following are the details of Sella's crystallographical determination:—

"System monoclinic:—

100, 101, = 17° 45′; 101, 001 = 20° 4′; 010, 111 = 57° 47′.

Forms observed:—

001, 110, $\bar{1}01$ (Fig. 64).

Combinations observed:—

001, 110 (Fig. 65).

Fig. 64.

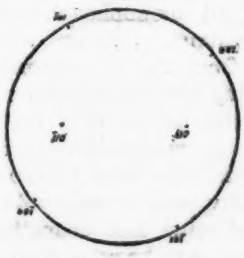


Fig. 65.

The face $\bar{1}\,0\,1$ has not been directly observed, but was found to be a cleavage. There is also another cleavage $0\,0\,1$, as distinct and easily obtained as $\bar{1}\,0\,1$."

The dibromide of hexmethylated ethylene-diphosphonium, treated with oxide of silver, yields the corresponding hydrate,

$$C_8H_{24}P_2O_2 = \left.\begin{matrix}[(C_2H_4)''(CH_3)_6P_2]'' \\ H_2\end{matrix}\right\}O_2,$$

which forms with acids a series of salts resembling the corresponding ethyl-compounds. Of these I have briefly examined the di-iodide and the platinum-salt.

Di-iodide.—The base, neutralized with hydriodic acid, furnishes a salt crystallized in difficultly soluble needles, surpassing in beauty the corresponding body in the ethyl-series.

Formula:—

$$C_8H_{22}P_2I_2 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P \\ (CH_3)_3P\end{matrix}\right]'' I_2,$$

Platinum-salt.—This is an apparently amorphous precipitate, which is nearly insoluble in water, dissolves with extreme slowness in boiling hydrochloric acid, and separates therefrom on cooling in golden-yellow laminæ, very much like those of the platinum-salt of the hybrid ethylene-trimethyl-triethyl-diphosphonium. It consists of

$$C_8H_{22}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P \\ (CH_3)_3P\end{matrix}\right]'' Cl_2,2PtCl_2.$$

Series of Mixed Diatomic Bases.

The investigation of the intimate relation which unites the bromethylated monophosphonium with the ethylene-diphosphonium-compounds, together with the establishment of the easy transition from the monatomic to the diatomic series, naturally suggested the idea of subjecting the bromethylated bromide, which forms the starting-point of the whole investigation, to the action of *monamines, monarsines,* and *monostibines,* in the expectation that diatomic bases would be formed containing nitrogen, arsenic, and antimony, side by side with phosphorus, and equivalent to it in chemical value and character. How far this expectation has been realized may be seen from the following experiments.

Phosphammonium-Compounds.

Action of Ammonia on Bromide of Bromethyl-triethylphosphonium.

In alcoholic solution, these two bodies act upon one another at ordinary temperatures, the reaction being indicated by considerable evolution of heat. To ensure complete transformation, the mixture is digested at 100° for half an hour in sealed tubes. On evaporating the alcohol and the excess of ammonia, there remains an extremely deliquescent saline mass, which crystallizes with difficulty. To remove small quantities of ammonia which may be present in the form of bromide of ammonium, the solution of the saline residue is treated with excess of oxide of silver, whereby a strongly alkaline liquid is set free, which may be digested on the water-bath without decomposition, so that traces of ammonia are easily driven off. Further investigation showed the presence in the caustic alkaline liquid of a base containing both phosphorus and nitrogen, viz. the hydrate of ethylene-triethylphosphammonium,

$$C_8H_{24}PNO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_3H_3PN]'' \\ H_2\end{matrix}\right\} O_2.$$

The reaction between the bromethylated monophosphonium and ammonia had therefore taken place exactly as might have been expected from the behaviour of the former compound with the monophosphines:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + H_3N = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ H_3\ N\end{matrix}\right]'' Br_2.$$

I have fixed the composition of the nitrophosphoretted base by the analysis of the platinum-salt and of the gold-salt.

Platinum-salt.—On saturating the alkaline hydrate with hydrochloric acid and adding dichloride of platinum, a very voluminous, pale-yellow, slightly crystalline precipitate is obtained, which is difficultly soluble in boiling water, and also in boiling concentrated hydrochloric acid. The acid solution deposits well-formed prismatic crystals. The crystallization from concentrated hydrochloric acid is necessary to ensure the purity of the product; it appears that the direct precipitate contains an admixture which remains dissolved in the acid.

Analysis led to the formula

$$C_8H_{22}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ H_3\ N\end{matrix}\right]'' Cl_2,2PtCl_2$$

Some of the crystals, obtained on slowly cooling a boiling solution in concentrated hydrochloric acid, were sufficiently well-formed to enable Q. Sella to examine them crystallographically. He has communicated to me the following description:—

"System trimetric:—

100, 110 = 59° 50′; 001, 101 = 70° 38′.

Forms observed:—

100, 110, 101. 010 (Fig. 66).

Fig. 66.

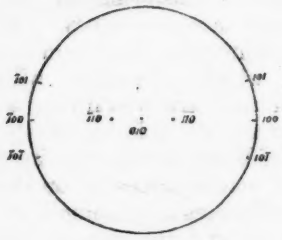


Fig. 67.

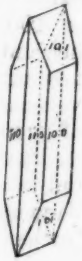


Fig. 68.

Combinations observed:—

100, 110, 101 (Fig. 67).

100, 110, 101; 010 (Fig. 68).

Cleavage 010 imperfect.

The faces 101 are dull, the others brilliant. The crystals are optically negative. The medium line is perpendicular to 100, and the plane of the optical axes is parallel to 001. The external angle of the optical axes appears to be about 60°.

Hardness greater than that of gypsum."

Gold-salt.—The solution of the dichloride, which is obtained by treating the crystallized platinum-salt with hydrosulphuric acid, yields with trichloride of gold a golden-yellow precipitate consisting of fine needles, which are difficultly soluble in water.

The formula of the salt is

$$C_8H_{22}PNAu_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\H_3\quad N\end{matrix}\right]''Cl_2,2AuCl_3$$

The analyses of the platinum-salt and of the gold-salt sufficiently fix the composition of the series of diatomic phosphammonium-compounds. I have prepared some of the simple salts of this nitrophosphoretted metal, especially the dichloride, the dibromide, and the di-iodide. They all crystallize pretty well, although they are in general more soluble and less stable than the diphosphonium-salts. The diperchlorate is rather difficultly soluble, and crystallizes with facility. These salts have not been analyzed. The free base likewise resembles the hydrate of the diphosphonium. Its solution is powerfully alkaline, and precipitates from most metallic salts the hydrates of the metals. The solution of the base may be concentrated on the water-bath without losing

ammonia; addition of potassa to the residuary liquid separates the hydrate in oily drops, which redissolve when mixed with water.

The peculiar construction of this body induced me to examine its deportment under the influence of heat. The substitution being limited to 5 equivs. of hydrogen, the question arose whether the hydrate could be distilled in the form of a phosphamine of the formula

$$\left.\begin{matrix}(C_2H_4)''\\(C_2H_5)_2\\(C_2H_5)H\end{matrix}\right\} PN.$$

Experiment showed, however, that the base cannot be volatilized without entire decomposition; the product of distillation no longer contains a trace of the original body. Ammonia is abundantly evolved during the distillation, and at a certain stage of the process the residue contains the *hydrate of vinylated triethylphosphonium*,

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_3H_3PN]''\\H_2\end{matrix}\right\} O_2 = H_3N + H_2O +$$
$$\left.\begin{matrix}[(C_2H_3)\ (C_2H_5)_3P]\\H\end{matrix}\right\} O.$$

I infer this from the analysis of an iodide obtained by neutralizing with hydriodic acid the mixed base which had been heated for some time. This salt was exceedingly soluble in water, and even in absolute alcohol; it was precipitated from the latter by addition of ether, and found to contain

$$C_8H_{18}PI = [(C_2H_3)\ (C_2H_5)_3P]I.$$

The mother-liquor of this salt was freed from excess of silver and precipitated by trichloride of gold. The yellow needles thus obtained were found to be the corresponding gold-salt

$$C_8\,H_{18}\,P\,Au\,Cl_4 = [(C_2H_3)\ (C_2H_5)_3\,P]\,Cl,\,Au\,Cl_3$$

The deportment of the bromethylated bromide under the influence of ammonia, opens an almost unlimited series of diatomic nitrophosphoretted metals. It is only necessary to replace in the above reaction the ammonia by a monamine, in order to obtain a new metal of almost any composition that could be desired. I have produced a few bodies of this description, in order to establish experimentally the relations, which theory, resting on the observations in the ammonia-reaction, sufficiently suggests.

Action of Methylamine on the Bromide of Bromethyl-triethylphosphonium.

Compounds of Ethylene-methyl-triethylphosphammonium.

Repetition of all the phenomena observed in the experiment with ammonia. Both substances unite on digestion,

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (CH_3)H_2N = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & P\\ (CH_3)H_2 & N\end{matrix}\right]''Br_2,$$

and the compound yields, on treatment with oxide of silver, the caustic base

$$C_9A_{26}PNO_2 = \left.\begin{matrix}[(C_2H_4)''(CH_3)(C_2H_5)_3H_2PN]''\\ H_2\end{matrix}\right\}O_2.$$

I have been satisfied to fix the composition of this body by the analysis of a rather difficultly soluble platinum-compound, crystallizing from boiling water in splendid needles, frequently an inch in length. I did not succeed, however, in obtaining, either from boiling water, or from boiling hydrochloric acid, crystals which could have been determined.

Formula:

$$C_9H_{24}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & P\\ (CH_3)H_2 & N\end{matrix}\right]''Cl_2, 2PtCl_2$$

Action of Ethylamine on the Bromide of Bromethyl-triethylphosphonium.

Compounds of Ethylene-tetrethylphosphammonium.

The two bodies unite with evolution of heat. Since the salts of the new phosphammonium crystallize very beautifully, I have not been able to resist the temptation of examining several of them somewhat more minutely.

Platinum-salt.—The crude product of the reaction, purified with oxide of silver and saturated with hydrochloric acid, furnishes, on addition of dichloride of platinum, an orange-yellow platinum-compound, crystallizing in needles very similar to those of the methyl-compound above-described. The salt, recrystallized from boiling water, has the composition

$$C_{10}H_{26}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & P\\ (C_2H_5)H_2 & N\end{matrix}\right]''Cl_2, 2PtCl_2.$$

Q. Sella has determined the crystalline form of this beautiful salt.

"System monoclinic:—

$100, 101 = 43°35'$; $101, 001 = 43°17'$; $111, 010 = 55°36'$.

Forms observed:—

100, 001, 110, 011 (Fig. 69).

Combinations observed:—

110, 011 (Fig. 70).
110, 011, 001 (Fig. 71).
110, 011, 001, 100 (Figs. 72, 73).

Fig. 69.

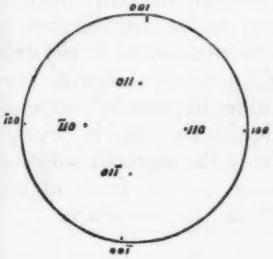


Fig. 70.

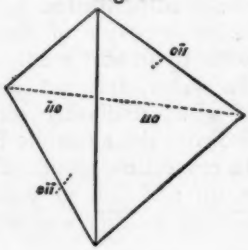


Fig. 71.

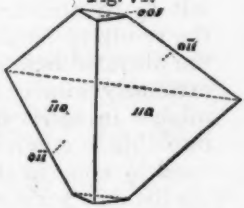


Fig. 72.

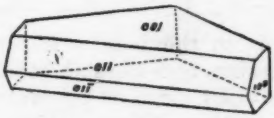
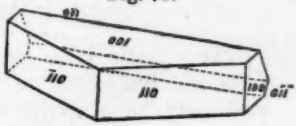


Fig. 73.



The crystals are hemihedral: the faces 001 and 100 have their parallels, but of the four faces of the forms 110 and 011 only two were observed with their corresponding parallels.

All the crystals examined exhibit the faces 110, $\bar{1}10$, and the faces $0\bar{1}1$, $0\bar{1}\bar{1}$ (Figs. 70, 71, and 73). In a single crystal (Fig. 72) the faces $\bar{1}\bar{1}0$, $1\bar{1}0$, and the faces 011, $01\bar{1}$ were observed. It is evident that the crystals Figs. 72 and 73 are symmetrical but not superposible.

The crystals frequently exhibit the habitus of triangular tables (Figs. 72 and 73); sometimes they are tetrahedrons (Fig. 70), or bevelled tetrahedrons (Fig. 71).

The faces are very brilliant but very often rounded, so that they are apt to yield many images and a great difference in the angles.

The plane of polarization is not altered if the light passes through the faces 001, $00\bar{1}$ and the faces 100, $\bar{1}00$ in the direction [010].

Colour orange-red.

The minuteness of the crystals, and the difficulty of fixing them on account of their hemihedral form, has prevented me from finding their cleavages."

Gold-salt.—Golden-yellow, difficultly soluble needles, which may be recrystallized from boiling water without decomposition.

Analysis led to the formula

$$C_{10}H_{26}PNAu_2Cl_8 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3 & P\\ (C_2H_5)H_2 & N\end{matrix}\right]'' Cl_2, 2AuCl_3.$$

Di-iodide.—It was prepared from the recrystallized platinum-salt by treatment with sulphuretted hydrogen, decomposition of the resulting dichloride by oxide of silver, and neutralization of the liberated base with hydriodic acid. White acicular crystals, extremely soluble in water, but not deliquescent, likewise very soluble in spirit of wine, difficultly soluble in absolute alcohol, insoluble in ether. From the alcoholic liquid, the salt is precipitated by ether in the crystalline state. From the aqueous solution, the iodide separates, on addition of potassa, in the form of oily globules, which gradually solidify with crystalline structure.

Formula:

$$C_{10}H_{26}PNI_2 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3 & P\\ (C_2H_5) & H_2N\end{matrix}\right]'' I_2.$$

The caustic base, which corresponds to the iodide, is readily obtained by oxide of silver. It presents considerable stability, and may be evaporated on the water-bath until it separates in heavy oily globules. Here again the action of heat might have given rise to the formation of a volatile phosphamine

$$\left.\begin{matrix}(C_2H_4)''\\ (C_2H_5)_2\\ (C_2H_5)_2\end{matrix}\right\} PN,$$

capable of reproducing the salts from which it was derived. But, exactly as in the case of the compound formed by the coalescence of triethylphosphine and ammonia, distillation destroys the base. The deportment of this substance under the influence of heat is characteristic; its study cannot fail to assist in the general elucidation of the constitution of this class of bodies. I may, in a subsequent inquiry, find an opportunity of returning to this question.

Both methylamine and ethylamine being primary monamines, I have, in conclusion, submitted the bromethylated bromide to the action of a secondary base, viz. diethylamine, and lastly, of some tertiary bases, viz. trimethylamine and triethylamine.

Action of Diethylamine on the Bromide of Bromethyl-Triethylphosphonium.

Compounds of Ethylene-pentethylphosphammonium.

The reaction is similar to that of ethylamine; the resulting product conveniently treated, yields a splendid platinum-salt crystallizing in rectangular plates, which contain

$$C_{12}H_{30}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_2HN\end{matrix}\right]''Cl, 2PtCl_2.$$

Action of Trimethylamine on the Bromide of Bromethyl-Triethylphosphonium.

Ethylene-trimethyl-triethylphosphammonium-compounds.

As to the preparation and properties, I may refer to the preceding paragraphs. The platinum-salt crystallizes in beautiful needles, of the composition,

$$C_{11}H_{28}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(CH_3)_3N\end{matrix}\right]''Cl_2, 2PtCl_2.$$

The examination of this compound has induced me to perform an experiment which may here be briefly mentioned. The action of trimethylamine on dibromide of ethylene gives rise to the formation of a beautifully crystallized salt, the bromide of bromethyl-trimethylammonium, of which I have already published a slight sketch in the 'Proceedings of the Royal Society'.* I was curious to ascertain whether the dibromide, generated by the union of *trimethylamine* with the bromide of bromethyl-*triethyl-phosphonium*, could likewise be formed by submitting the bromide of bromethyl-*trimethylammonium* to the action of *triethylphosphine*:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (CH_3)_3N = [(C_2H_4Br)(CH_3)_3N]Br +$$
$$(C_2H_5)_3P = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(CH_3)_3N\end{matrix}\right]''Br_2.$$

The bromide of bromethylated trimethylammonium is indeed readily attacked by triethylphosphine, but the change is very different from what I had expected. I intend in another paper to return to the products of this reaction.

Before leaving the history of the phosphammonium-compounds, I have briefly to allude to a peculiar deportment of the bromethylated bromide. When treating this compound with triethylamine,

* Proceedings of the Royal Society, vol. ix. p. 293.

instead of trimethylamine, expecting, of course, to observe a repetition of the phenomena so frequently witnessed, I was surprised to find that these substances, although acting with considerable energy, failed to produce the anticipated phosphammonium-compound. This unforeseen result induced me to examine this reaction repeatedly and with particular care. The result remained the same. On evaporating the alcoholic product of the reaction, and treating the concentrated solution with oxide of silver, a powerfully alkaline liquid remained, even after the expulsion of the triethylamine, considerable quantities of which were liberated. This residuary alkaline liquid, saturated with hydrochloric acid, yielded, on addition of dichloride of platinum, the beautiful octohedra of the oxethylated triethylphosphonium-platinum-salt, which was identified by analysis.

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3N + H_2O = [(C_2H_5O)(C_2H_5)_3P]Br + [(C_2H_5)_3HN]Br.$$

This equation involves the intervention of water in the reaction, which was obviously furnished by the imperfectly de-hydrated alcohol used in the experiments. In the anhydrous state, the bromethylated bromide and triethylamine scarcely act at 100°; between 120° and 130°, a reaction takes place, among the products of which, as yet very imperfectly examined, I was likewise unable to trace the presence of a phosphammonium-like-compound. It can scarcely be doubted that this reaction gives rise to the formation of bromide of vinyl-triethylphosphonium:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3N = [(C_2H_3)(C_2H_5)_3P]Br + [(C_2H_5)_3HN]Br.$$

Experimentally the question remains undecided.

The elegance and precision with which the bromethylated bromide fixes the elements of ammonia and of the monamines, very naturally suggested the idea of examining the deportment of this body under the influence of diamines and triamines. The results obtained in these experiments do not belong to this part of the inquiry. Suffice it to say for the present, that these substances attack the bromide with the utmost energy, giving rise to an almost unlimited number of polyatomic bases of a higher order, the constitution of which, though complicated, is traceable in advance by the experience acquired in the simpler forms of reaction.

Phospharsonium-Compounds.

There was no necessity for entering into a detailed examination of this class of compounds. I have in fact been satisfied to

establish, by a few characteristic numbers, the existence of the phospharsonium-group.

Action of Triethylarsine on the Bromide of Bromethyl-triethylphosphonium.

On digesting the two substances in sealed tubes, the usual phenomena are observed. The saline mass which is formed yields, by treatment with oxide of silver *in the cold*, a powerfully alkaline solution, containing the *dihydrate of ethylene-hexethylphospharsonium*,

$$C_{14}H_{36}PAsO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6PAs]'' \\ H_2\end{matrix}\right\} O_2.$$

It is thus obvious that arsenic-base imitates triethylphosphine in its deportment with the bromethylated bromide. The two substances simply combine to form the dibromide of the phospharsonium.

The alkaline solution of the hydrate of the phospharsonium exhibits the leading characters of this class of bases; I may therefore refer to the detailed account which I have given of the hydrate of the diphosphonium. The saline compounds likewise resemble those of the diphosphonium. The dichloride and the di-iodide were obtained in beautiful crystalline needles, exhibiting a marked tendency to form well-crystallized double salts. I have prepared the compounds of the dichloride with chloride of tin, bromide of zinc, trichloride of gold, and lastly, with dichloride of platinum. The latter compound was analysed in order to fix the composition of the series.

Platinum-salt.—The product of the reaction of triethylarsine upon the bromethylated bromide is treated with oxide of silver *in the cold*, and the alkaline solution thus obtained is saturated with hydrochloric acid, and precipitated with dichloride of platinum. An exceedingly pale yellowish, apparently amorphous precipitate of marked diphosphonic appearance is thrown down, almost insoluble in water, but dissolving in boiling concentrated hydrochloric acid. The hydrochloric solution deposits, on cooling, beautiful orange-red prisms, resembling the crystals of the corresponding diphosphonium-platinum-salt.

Formula:

$$C_{14}H_{34}PAsPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ (C_2H_5)_3As\end{matrix}\right]''Cl_2, 2PtCl_2.$$

Quintino Sella has examined the crystals of the phospharsonium-platinum-salt. I append the results of his observations.

"System triclinic:—

$100, 010 = 81° 52'$; $100, 001 = 88° 14'$;
$010, 001 = 89° 9'$; $100, \bar{1}11 = 120° 18'$;
$010, \bar{1}11 = 64° 4'$.

Forms observed:—

100, 001, 010, 011, $\bar{1}11$, $02\bar{1}$ (Fig. 74).

Combinations:—

100, 010, 001 (Fig. 75).

100, 010, 001; $\bar{1}11$ (Fig. 76).

100, 010, 001; $\bar{1}11$, $02\bar{1}$

100, 010, 001; $\bar{1}11$, $02\bar{1}$, 011 (Fig. 77).

Fig. 74.

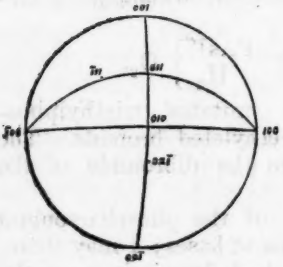


Fig. 75.

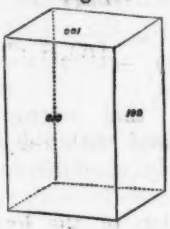


Fig. 76.

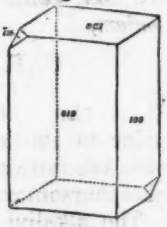


Fig. 77.

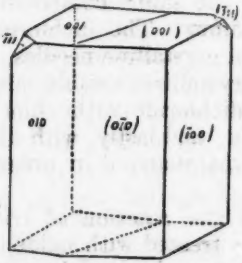
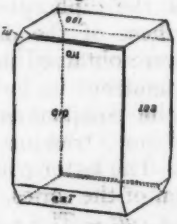


Fig. 78.



Cleavages 100 and 001: distinct and easily obtained. The cleavage is occasionally observed to take place during measuring, probably in consequence of the heat emanating from the face, which has to be brought close on account of the minuteness of the crystals.

Hemitropic crystals with the axis of hemitropy [001] (Fig. 78). It was possible to verify by measurement that the axis of hemitropy is really [001], and not a line perpendicular to one of the faces of the crystal."

The phospharsonium-compounds, and more especially the hydrate of the series, are far less stable than the corresponding terms of the diphosphonium-series.

If the product of the action of triethylarsine on the bromethylated monophosphonium be *boiled* with oxide of silver, instead of being treated in the cold, not a trace of the phospharsonium-compound is obtained. The caustic solution which is formed,

yields, when saturated with hydrochloric acid and precipitated with dichloride of platinum, only the rather soluble octohedral crystals of the oxethylated triethylphosphonium. The nature of this transformation is clearly exhibited when a solution of the hydrate of the phospharsonium, filtered off *in the cold* from the excess of oxide of silver, is submitted to ebullition. Immediately the clear liquid is rendered turbid from separated triethylarsine, which becomes perceptible, moreover, by its powerful odour; the solution now contains the hydrate of oxethylated triethylphosphonium.

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6PAs]'' \\ H_2\end{matrix}\right\}O_2 = (C_2H_5)_3As + \left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P] \\ H\end{matrix}\right\}O$$

When the dibromide is boiled with the oxide of silver, a beautiful silver mirror is formed on the sides of the vessel, obviously in consequence of a partial oxidation of the liberated triethylarsine.

Some experiments were made to produce a diatomic compound containing phosphorus and antimony. I expected to form this body, the dibromide of a phosphostibonium, by the action of triethylstibine on the bromethylated bromide, so frequently mentioned in this paper. The two bodies react upon one another, but only after protracted digestion or exposure to a rather high temperature. The product of the reaction is complex, yielding a comparatively small quantity of a difficultly soluble platinum-salt of diatomic appearance. I have repeatedly modified the reaction, and analysed the products in the form of platinum-salts; I omit to quote the detail of these experiments, since they have failed to disentangle the difficulties of the reaction.

Some experiments upon the deportment of dibromide of ethylene with triethylarsine were more successful. The reaction between these two bodies had been selected as a subject of inquiry by Mr. W. Valentin, to whom I am indebted for valuable assistance in the earlier stages of these researches. Circumstances have subsequently prevented Mr. Valentin from carrying out his plan, and I have therefore to take upon myself the responsibility for the following statements. The results obtained in the examination of the arsenic-compounds are by no means absolutely connected with the study of the phosphorus-bases; nevertheless I may be permitted to lay them before the Society, together with the account of the corresponding reaction in the phosphorus-series.

Monarsonium-Compounds.

Action of Dibromide of Ethylene upon Triethylarsine.

The experience gathered during the examination of the phosphorus-bodies enabled me to establish the nature of this reaction by a comparatively small number of platinum-determinations.

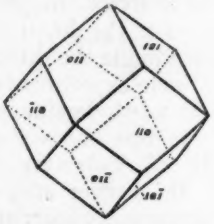
Bromide of Bromethyl-triethylarsonium.—To avoid, as far as possible, the formation of the second product, a mixture of triethylarsine with a very large excess of dibromide of ethylene was digested in sealed tubes, at a temperature not exceeding 50° C. Notwithstanding this low temperature, the tubes invariably contained compressed gases. The product of the reaction was treated with water, which extracted a soluble bromide from the ethylene-compound unacted upon. On evaporation, a beautiful bromide was left, which, being copiously soluble in boiling, and sparingly soluble in cold alcohol, could be readily recrystallized from absolute and even from common alcohol. In water this substance is excessively soluble; it is, therefore, scarcely crystallizable from an aqueous solution.

Analysis, as might have been expected, proved this salt to be the analogue of the bromethylated triethylphosphonium-salt. It contains

$$C_8H_{19}AsBr_2 = [(C_2H_4Br)(C_2H_5)_3As]Br.$$

The bromide of bromethyl-triethylarsonium can be obtained in beautiful crystals. Their form—the rhombic dodecahedron—is identical with that of the corresponding bromethyl-triethylphosphonium-compound, which the crystals resemble also in their general habitus. They were measured by Q. Sella.

Fig. 79.



"System monometric.

Forms observed:—

110 (Fig. 79).

No influence on polarized light."

Platinum-salt.—The solution of the previous salt, converted by treatment with chloride of silver into the corresponding chloride, yields with dichloride of platinum splendid needles of a double salt, difficultly soluble in cold and even in boiling water, containing—

$$C_8H_{19}BrAsPtCl_3 = [(C_2H_4Br)(C_2H_5)_3As]Cl,PtCl_2.$$

Compounds of Vinyl-triethylarsonium.

The bromide of bromethyl-triethylarsonium, like the corresponding phosphorus-compound, loses its latent bromine under the influence of oxide of silver. If the solution of the bromide be precipitated by an excess of nitrate of silver, one-half of the bromide separates as bromide of silver; the clear filtrate, mixed with ammonia, yields the second half of the bromine in the form of a dense precipitate. Nevertheless the reaction differs from that observed in the phosphorus-series. The bromide of the bromethylated phosphonium, as has been pointed out in a former part of this inquiry, is almost invariably converted into an oxethylated body, its transformation into a vinyl-compound being altogether exceptional. The bromide of the bromethylated arsonium, on the other hand, yields, as a rule, the vinyl-body of the series, the formation of an oxethylated compound taking place only under particular circumstances; in fact so rarely as to leave some doubt regarding the existence of this term of the series. The bromide of the bromethylated arsonium, treated with an excess of oxide of silver, yields a powerfully alkaline solution, the nature of which was determined by the analysis of the corresponding platinum-salt. Transformed into the chloride, and precipitated by dichloride of platinum, this solution yielded beautiful rather soluble octohedra of the formula:

$$C_8 H_{18} As Pt Cl_3 = [(C_2 H_3)\ (C_2 H_5)_3 As]\ Cl, Pt Cl_2.$$

Gold-salt.—The chloride obtained in the analysis of the platinum-salt, gives with trichloride of gold a yellow, difficultly soluble, faintly crystalline precipitate of the formula:

$$C_8 H_{18} As Au Cl_4 = [(C_2 H_3)\ (C_2 H_5)_3 As]\ Cl, Au Cl_3.$$

These results show that the transformation of the bromethylated compound ensues according to the following equation:—

$$[(C_2 H_4 Br)\ (C_2 H_5)_3 As]\ Br + \left.\begin{matrix} Ag \\ Ag \end{matrix}\right\} O = 2\ Ag Br + \left.\begin{matrix} [(C_2 H_3)(C_2 H_5)_3 As] \\ H \end{matrix}\right\} O.$$

The idea suggested itself that the vinyl-compound obtained in this reaction might be a secondary product resulting from the decomposition of an oxethylated compound of limited stability formed in the first instance:—

$$\left.\begin{matrix} [(C_2 H_5 O)\ (C_2 H_5)_3 As] \\ H \end{matrix}\right\} O = \left.\begin{matrix} H \\ H \end{matrix}\right\} O + \left.\begin{matrix} [(C_2 H_3)\ (C_2 H_5)_3 As] \\ H \end{matrix}\right\} O.$$

It was with the view of avoiding this decomposition, that in some of the experiments, the digestion was accomplished at the common temperature; the result, however, showed that even in these cases the vinyl-compound was obtained.

Nevertheless the oxethylated body appears to exist. Under circumstances which were not sufficiently well observed at the time, the action of oxide of silver upon the bromide of the bromethylated triethylarsonium yielded an octohedral platinum-salt with the platinum percentage of the oxethylated compound:

$$[(C_2H_5O)(C_2H_5)_3As]Cl, PtCl_2.$$

Diarsonium-Compounds.

Dibromide of Ethylene-hexethyl-diarsonium.—The bromide or chloride of the bromethylated arsonium is but slowly acted upon by triethylarsine at 100° C. Two days' digestion at that temperature had produced but a slight impression; at 150° the reaction is accomplished in two hours. The phenomena now to be recorded presented themselves in the succession repeatedly observed in the phosphorus-series. The dibromide

$$C_{14}H_{34}As_2Br_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Br_2$$

yielded, when debrominated, the powerful alkali

$$C_{14}H_{36}As_2O_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6As_2]''\\H_2\end{matrix}\right\}O_2.$$

Treated with acids, this alkali produces a series of fine salts, amongst which the di-iodide deserves to be mentioned; it equals in beauty the corresponding diphosphonium-compound. I have fixed the composition of the series by the analysis of the platinum-salt and gold-salt.

Platinum-salt.—Pale yellow crystalline precipitate, similar to the diphosphonium-compound, difficultly soluble in water, soluble in boiling concentrated hydrochloric acid, from which it crystallizes on cooling.

Formula:

$$C_{14}H_{34}As_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Cl_2,2PtCl_2$$

Gold-salt.—The dichloride obtained after separating the platinum in the analysis of the platinum-salt by means of sulphuretted hydrogen, was precipitated by trichloride of gold. Yellow slightly

crystalline precipitate, soluble in hydrochloric acid, from which it separates in golden-coloured plates of the composition,

$$C_{14}H_{34}As_2Au_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Cl_2,2AuCl_3$$

Arsammonium-compounds.

Bromide of bromethylated triethylarsonium, as might have been expected, is capable of fixing ammonia and the monamines, giving rise to the formation of a series of compounds not less numerous than that of the bodies mentioned in the phosphammonium-series. I have been satisfied to study the action of ammonia upon the bromide.

Dibromide of Ethylene-triethylarsammonium.—Reaction complete in two hours at 100°.

The product contained the bromide

$$C_8H_{22}AsNBr_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\H_3\quad N\end{matrix}\right]''Br_2.$$

which was converted, by means of oxide of silver, into the stable caustic base

$$C_8H_{24}AsNO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_3H_3AsN]''\\H_2\end{matrix}\right\}O_2,$$

the composition of this base which was determined by the analysis of the platinum- and gold-salts.

Platinum-salt.—Needles difficultly soluble in boiling water, soluble in boiling concentrated hydrochloric acid, from which well-formed crystals are deposited.

Formula:

$$C_8H_{22}AsNPt_2Cl_6 = \left[C_2H_4)''\begin{matrix}(C_2H_5)_3As\\H_3\quad N\end{matrix}\right]''Cl_2,2PtCl_2,$$

Gold-salt.—Yellow compound precipitated from the dichloride obtained in the analysis of the platinum-salt, on adding a solution of trichloride of gold. Soluble in hydrochloric acid; deposited from this solution in golden-yellow plates, containing

$$C_8H_{22}AsNAu_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\H_3\quad N\end{matrix}\right]''Cl_2,2AuCl_3$$

I have also made a few experiments on the action of dibromide of ethylene upon triethylstibine. The reaction is slow, and required long-continued digestion at temperatures higher than that of boiling water. The tubes invariably contained much gas, and the product of the reaction proved to be an inattractively complex mixture of several compounds, many of them secondary,

which by no means invited me to a more minute examination of this process. I omit to quote the few platinum- and chlorine-determinations which were made, since they do not admit of a simple interpretation.

In performing the experiments on the arsenic-bases I have been most ably assisted by my nephew, Dr. P. W. Hofmann, to whom I express my best thanks for his active co-operation in this part of my inquiries.

The experiments carried out in the ethylene-series, develope clearly enough the nature of the diatomic bases, and their relation to the monatomic compounds. I have worked with predilection in this series, because the accesibility and manageableness of the material greatly facilitate the unravelling of the often complicated reactions. There could be no doubt that the phenomena observed in the ethylene-series would likewise be reproduced in other homologous series. But as a general view of the nature of this group of bodies had been gained from the observations recorded in the preceding paragraphs, it appeared scarcely necessary to corroborate the results already obtained, by many further experiments, which would have been more or less mere repetitions of the former. Nevertheless I have, in certain cases, drawn other groups into the circle of my observations. Some of the fragmentary results at which I thus arrived I will here briefly communicate.

Methylene-Group.

In another place* I have mentioned an experiment made in the hope of converting iodoform into iodide of carbon, which, however, yielded nothing but the di-iodide of methylene, discovered not long previously by Boutlerow. As a considerable quantity of this interesting compound (the result of these experiments) was still at my disposal, I took the opportunity of examining more particularly its behaviour to triethylphosphine and the ammonias in general.

The methylenated derivatives of the phosphorus-bases will be more conveniently examined in connexion with another class of compounds, to which a special chapter of this inquiry must be devoted. I will therefore only briefly mention in this place, that I have succeeded in producing several of the bases belonging to the methylene-group. The members of this series present some peculiarities, distinguishing them in a marked manner from the corresponding ethylene-compounds.

* Journal of the Chemical Society, vol. xiii, p. 65.

Propylene and Amylene-Groups.

The experiments in the propylene- and amylene-groups were instituted almost at the beginning of this investigation, at a time when the reaction between triethylphosphine and dibromide of ethylene had not yet been sufficiently disentangled. The removal of the difficulties in the ethylene series has naturally cooled my interest in the corresponding reactions of the propylene- and amylene-series, and hence this part of the investigation has been left incomplete.

Triethylphosphine is briskly attacked by the dibromides, both of propylene and amylene; the reactions, however, do not exhibit the welcome simplicity and smoothness which characterize those in the ethylene-series. Even in the propylene-compound, whether it be prepared from amylic alcohol or from iodide of allyl, we miss with regret the sharply defined characters of the corresponding ethylene-body; and in the butylene-, and still more in the amylene-series, these features become fainter and fainter.

When submitted to the action of the dibromides of propylene and amylene, triethylphosphine appears to undergo simultaneously two different sets of changes, the substances formed being partly direct products of the reaction, partly and perhaps chiefly, indirect products. The diphosphonium-compounds of the propylene- and amylene-series are less stable than the ethylene-diphosphoniums, and are therefore always mixed with such products of decomposition as are formed in the ethylene-group only under the protracted influence of high temperatures. Under all circumstances, however, these dibromides give up the elements of hydrobromic acid, so that we have to eliminate a painfully small quantity of the searched-for products from an unprofitable mass of bromide of triethylphosphonium. In such cases the ordinary methods of separation no longer suffice, and we are compelled to resort to treatment with baryta, the real examination of the products beginning only after the liberated phosphorus-base has been removed by ether, and the bromide of barium decomposed by means of oxide of silver and carbonic acid. By this treatment, beautiful iodides and platinum-salts are obtained, which, however, have as yet been but partially and imperfectly investigated.

Phenylene-Group.

Unfortunately nothing but fruitless experiments. I had hoped to find in triethylphosphine a bridge between the phenyl- and the phenylene-series, but my expectations have not been realized. The analogy between the salts of bromethylated triethylphosphonium and of bromophenylated ammonium

$$\begin{matrix}[(C_2H_4Br)\ (C_2H_5)_3P\ ]Br,\\ [(C_6H_4Br)\quad H_3\ \ N]Br,\end{matrix}$$

is unmistakeable, and it remained to be seen whether triethylphosphine would attack the salts of bromophenylammonium according to the equation

$$[(C_6H_4Br)H_3N]Br + (C_2H_5)_3P = \left[(C_6H_4)''\begin{matrix}(C_2H_5)_3P\\ H_3\ N\end{matrix}\right]'' Br_2.$$

Unfortunately the mixture of the two bodies is not changed even after being heated for some time to 160°. No better result was obtained by substituting for the bromophenylamine, the corresponding iodinated base. A mixture of triethylphosphine and iodophenylamine, which had been kept for a day at 160°, yielded, on opening the tube, an appreciable quantity of iodine, recognizable by silver-salts, but the decomposition was by no means complete. Hydriodic acid separated from the mixture an iodide which crystallized in long needles, and was found by analysis to consist of iodide of iodophenylammonium. In the products of transformation of the phosphorus-base I was unable to trace the simple relations pointed out by theory.

Benzylene-Group.

In conclusion, I will mention a few experiments upon the mutual reaction between triethylphosphine and dichloride of benzylene. By this latter name I denote the compound, discovered by Cahours, which is produced by the action of pentachloride of phosphorus on bitter almond oil.

At ordinary temperatures, and even at 100°, the two compounds react but slowly upon each other; between 120° and 130°, however, especially in presence of alcohol, the change takes place with facility. The resulting crystalline mass, like that obtained in the corresponding experiments in the propylene- and amylene-series, consists chiefly of chloride of triethylphosphonium. After removing the phosphorus-base as completely as possible from the solution of the crystals, by the successive treatment with baryta, oxide of silver, and carbonic acid, there remained a strongly alkaline liquid, the nature of which I endeavoured to determine by the preparation of the iodide and platinum-salt. The liquid, saturated with hydriodic acid, yielded a well-crystallized iodide, which, however, was so soluble and deliquescent that no constant results could be obtained by its analysis. On the other hand, the somewhat sparingly soluble platinum-salt, which is precipitated in small laminæ, on treating the solution of the chloride with dichloride of platinum, and may be recrystallized without alteration from boiling water, yielded results agreeing with one another, although the products of different preparations were submitted to analysis.

These analyses led to the formula

$$C_{13}H_{22}P\ PtCl_3 = [(C_2H_5)_3(C_7H_7)P]Cl,\ PtCl_2.$$

The transformation of triethylphosphine under the influence of dichloride of benzylene, evidently takes place according to the following equation:

$$3[(C_2H_5)_3P] + C_7H_6Cl_2 + H_2O = [(C_2H_5)_3HP]Cl + [(C_2H_5)_3(C_7H_7)P]Cl + (C_2H_5)_3PO.$$

It may be that the formation of the triethyl-benzylphosphonium-compound is preceded by the production of an ephemeral diatomic base containing the radical C_7H_6,

$$2[(C_2H_5)_3P] + C_7H_6Cl_2 = \left[(C_7H_6)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' Cl_2,$$

which is subsequently decomposed under the joint influence of water and an excess of triethylphosphine. I have not, however, been able, experimentally, to trace this base. Moreover, a difference in the deportment of triethylphosphine with the compounds of ethylene and benzylene is readily intelligible, if we recollect that they are far from being analogous, dichloride of benzylene representing in the benzyl-group the diatomic derivatives which have been obtained from ethylic aldehyde.

The analysis of the benzyl-triethylphosphonium-platinum-salt concludes the experimental part of this section of my researches.

The following Table exhibits at a glance the several groups of bodies examined in Parts II. and III. of this inquiry.

MONATOMIC-COMPOUNDS. PHOSPHORUS-GROUP.

Monophosphonium-salts. Ethyl-series.

Salt of Tetrethylphosphonium	$[(C_2H_5)_4P]Br.$
Salt of Bromethyl-triethylphosphonium	$[(C_2H_4Br)(C_2H_5)_3P]Br.$
Salt of Chlorethyl-triethylphosphonium	$[(C_2H_4Cl)(C_2H_5)_3P]Br.$
Salt of Oxethyl-triethylphosphonium	$[(C_2H_4HO)(C_2H_5)_3P]Br.$
Salt of Vinyl-triethylphosphonium	$[(C_2H_3)(C_2H_5)_3P]Br.$

Ethyl-methyl-series.

Salt of Ethyl-trimethylphosphonium	$[(C_2H_5)(CH_3)_3P]Br.$
Salt of Bromethyl-trimethylphosphonium	$[(C_2H_4Br)(CH_3)_3P]Br.$
Salt of Oxethyl-trimethylphosphonium	$[(C_2H_4HO)(CH_3)_3P]Br.$

Ethyl-benzyl-series.

Salt of Triethyl-benzylphosphonium	$[(C_2H_5)_3(C_7H_7)P]Br.$

ARSENIC-GROUP.

Monarsonium-salts. Ethyl-series.

Salt of Tetrethylarsonium . . $[(C_2H_5)_4As]Br.$
Salt of Bromethyl-triethylarsonium $[(C_2H_4Br)(C_2H_5)_3As]Br.$
Salt of Vinyl-triethylarsonium . $[(C_2H_3)(C_2H_5)_3As]Br.$

DIATOMIC-COMPOUNDS. PHOSPHORUS-GROUP.

Diphosphonium-salts.

Salt of Ethylene-hexethyldiphosphonium . . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$

Salt of Ethylene-trimethyl-triethyldiphosphonium . . . . $\left[(C_2H_4)''\begin{matrix}(C\ H_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$

Salt of Ethylene-hexmethyldiphosphonium . . . . . $\left[(C_2H_4)''\begin{matrix}(C\ H_3)_3P\\(C\ H_3)_3P\end{matrix}\right]''Br_2.$

ARSENIC-GROUP.

Diarsonium-salts.

Salt of Ethylene-hexethyldiarsonium $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Br_2.$

PHOSPHORUS-NITROGEN-GROUP.

Phosphammonium-salts.

Salt of Ethylene-triethylphosphammonium . . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\H_3\ \ N\end{matrix}\right]''Br_2.$

Salt of Ethylene-methyl-triethylphosphammonium . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(CH_3)H_2N\end{matrix}\right]''Br_2.$

Salt of Ethylene-tetrethylphosphammonium . . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)H_2N\end{matrix}\right]''Br_2.$

Salt of Ethylene-pentethylphosphammonium . . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_2HN\end{matrix}\right]''Br_2.$

Salt of Ethylene-trimethyl-triethylphosphammonium . . . $\left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3N\end{matrix}\right]''Br_2.$

PHOSPHORUS-ARSENIC-GROUP.

Phospharsonium-salts.

Salt of Ethylene-hexethylphosparsonium . . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3As\end{matrix}\right]''Br_2.$

ARSENIC-NITROGEN-GROUP.

Arsammonium-salts.

Salt of Ethylene-triethylarsammonium . . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3\ As\\H_3\ \ \ N\end{matrix}\right]''Cl_2.$

The experiments described in the preceding pages refer almost exclusively to the study of compounds belonging either to the phosphorus-series or to the phosphorus-nitrogen-series. Numerous analogous terms of the nitrogen-series, monatomic as well as diatomic, with which I have become acquainted in the course of my researches, have been left unnoticed in this paper. I propose to examine the nitrogen-bodies in a special memoir; and I may here only remark, that these substances, although differing in several points, nevertheless so closely imitate, in their general deportment, the corresponding terms of the phosphorus-series, that the picture which in the preceding pages I have endeavoured to delineate of the phosphorus-compounds, illustrates, in a great measure, the deportment of the nitrogen-bodies. We meet here with the peculiar case of the study of the phosphorus-group being in advance of that of the nitrogen-series, whilst generally the investigation of the phosphorus-compounds was taken in hand only after inquiries in the nitrogen-series had furnished the prototypes to be copied.

In conclusion, a few words about the further development of which the experiments described appear to be capable, and about the direction in which I propose to pursue the opened track.

Conceived in its simplest form, the transition from the series of monatomic to that of diatomic bases may be referred to the introduction of a monochlorinated or monobrominated alcohol-radical into the ammonium-nucleus, the chlorine or bromine thus inserted furnishing the point of attack for a second molecule of ammonia. If in bromide of ethylammonium we imagine 1 equiv. of hydrogen in ethyl replaced by bromine, we arrive at the bromide of bromethyl-ammonium, which is capable of fixing a second molecule of ammonia, and of being thus converted into the dibromide of ethylene-diammonium, the latent bromine becoming accessible to silver-salts:

$$[(C_2H_4Br)H_3N]Br + H_3N = [(C_2H_4)''H_6N_2]''Br_2.$$

The further elaboration of this reaction suggests two different methods for the construction of polyatomic bases of a higher order. In the first place, the number of ammonia-molecules to be incorporated in the new system may be increased by the gradually advancing bromination of the radical. By the further bromination of ethyl in bromide of bromethyl-ammonium and the action of ammonia on the bodies thus produced, the following compounds might be generated:—

$$[(C_2H_3Br_2)H_3N]Br + 2H_3N = [(C_2H_3)''' \quad H_9N_3]''' \quad Br_3.$$
$$[(C_2H_2Br_3)H_3N]Br + 3H_3N = [(C_2H_2)'''' \quad H_{12}N_4]'''' \quad Br_4.$$
$$[(C_2HBr_4)H_3N]Br + 4H_3N = [(C_2H)''''' \quad H_{15}N_5]''''' \quad Br_5.$$
$$[(C_2Br_5) \quad H_3N]Br + 5H_3N = [(C_2 \quad)''''' \quad H_{18}N_6]''''' \quad Br_6.$$

Again the fixation of the ammonia-molecules might be attempted, not by the progressive bromination of the ethyl, but by the accumulation of monobrominated ethyl-radicals in the ammonium-nucleus. The bromide of the di-bromethylammonium, when submitted to the action of ammonia, would thus yield the tribromide of a triammonium, the bromide of tri-bromethylammonium, the tetrabromide of a tetrammonium; and, lastly, the bromide of tetra-bromethylammonium, the pentabromide of a pentammonium.

$$[(C_2H_4Br)_2H_2N]Br + 2H_3N = [(C_2H_4)_2'' H_8 N_3]''' Br_3.$$
$$[(C_2H_4Br)_3H N]Br + 3H_3N = [(C_2H_4)_3'' H_{10}N_4]'''' Br_4.$$
$$[(C_2H_4Br)_4 N]Br + 4H_3N = [(C_2H_4)_4'' H_{12}N_5]''''' Br_5.$$

As yet the bromination of the alcohol-bases presents some difficulty; appropriately selected reactions, however, will doubtless furnish these bodies. They will probably be obtained by indirect means, similar to those by which, years ago, I succeeded in preparing the chlorinated and brominated derivatives of phenylamine; or these substances may be generated by the action of pentachloride and pentabromide of phosphorus upon the oxethylated bases, a process which, from the few experiments recorded in this memoir, promises a rich harvest of results.

I have but faint hope that I may be able to trace these new paths to their goal; inexorable experiment follows but slowly the flight of light-winged theory. The commencement is nevertheless made, and even now the triammonium- and tetrammonium-compounds begin to unfold themselves in unexpected variety.

I conclude this memoir with the expression of my best thanks for the untiring patience with which Mr. Peter Griess has assisted me in the performance of my experiments on the phosphorus-bases. The truly philosophical spirit in which this talented chemist has accompanied me throughout the varying fortunes of this inquiry, will always be one of my most pleasing recollections.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 17th, 1861.

Alfred Smee, Esq., Vice-President, in the Chair.

James Apjohn, M.D., Professor of Chemistry, Trinity College, Dublin, was elected a Fellow of the Society; and Arthur Reynolds, Esq., Royal Arsenal Laboratory, Woolwich, was elected an Associate of the Society.

The following papers were read:—

"Analysis of the Saline Water of Purton, near Swindon," by Dr. Noad, F.R.S.

"On the Composition of Purton Water," by Dr. Voelker.

"On the Electrolytic test for Arsenic," by Professor Bloxam.

"On a new Silver-phosphonium-compound," by Dr. Hofmann, F.R.S.

February 7, 1861.

Professor Brodie, President, in the Chair.

The following were elected Fellows of the Society:—

John Davis, Esq., 20, Princes-street, Spitalfields; Charles Edward Beadnell, Esq., West Green-road, Tottenham.

The following were elected Associates of the Society:—

Dr. Charles Ulrich, 40, London-street: Edouard Louis Barrett, St. Bartholomew's Hospital.

The following papers were read:—

"On the Carbonates of Copper, Cobalt, and Nickel," by Mr. Frederick Field.

"On the Oxidation of Benzol," by Mr. A. H. Church.

February 21, 1861.

Dr. Warren De la Rue, Treasurer, in the Chair.

The following were elected Fellows of the Society:—

James Napier, Junior, Esq., 5, New Broad-street Buildings; William Weston, Esq., Museum of Practical Geology; Dr. Murray Thomson, Lecturer on Chemistry, Glasgow.

The following papers were read:—

"On the action of dilute Nitric Acid upon some Hydrocarbons of the Benzol series," by Warren de la Rue, M.D., and H. Müller.

"On the Putrefaction of Bile, and Formation of Gall-stones," by Dr. Thudichum.

"On the Bisulphide of Iodine," by Dr. Guthrie.

"On Ground Ice," by Mr. R. Adie.

March 7, 1861.

Dr. Hofmann, Foreign Secretary, in the Chair.

J. J. Coleman, Esq., Commercial College, Halifax, was elected a Fellow of the Society.

A paper was read,—

"On some Minerals from Chile," by Mr. Frederick Field.

Dr. Hofmann, made a verbal communication "On Mr. Griess's further researches upon Nitrogen-substitutions."

March 21, 1861.

Professor Brodie, President, in the Chair.

The following were elected Fellows of the Society:—

William Vazie Simons, Esq., 10, Avenue-road, Hammersmith; Edwin Burton Brown, M.D., Medical College, Lahore; Henry Owen Huskisson, Esq., 30, Mecklenburgh-square; Adam Clarke McLean, B.A., Wesleyan College, Taunton.

Professor Williamson delivered a discourse "On Thermodynamics in relation to Chemical Affinity."

Anniversary Meeting, March 30, 1861.

Professor Brodie, President, in the Chair.

The following Report of the Council, and the Audited Account of the Treasurer, were read:—

It is the custom at the Annual Meeting to lay before the Society a brief statement as to its progress.

The number of Fellows at the last annual meeting was 323; during the past year there has been an increase of 19, making the present number 342. The number of Associates is at present 10, being 2 less than the number of last year.

The increase of the Fellows of the Chemical Society is, to some extent, a measure of the interest felt in this country in the Science of Chemistry, and of the number of its cultivators. We may, therefore, observe with gratification, that the number of Fellows of our Society is steadily on the increase. Comparing the progress of the Society for the last 5 years, we find that from the year 1845 to 1850, the Society increased by 24 members, or 4·8 annually; from 1850 to 1856 (a period of 6 years) there was an increase of 35 members, or 5·8 annually; while from 1856 to 1861, there has been an increase of 86 members, or 17·4 annually, the rate of increase in the five years from 1856 to 1861 being more than three times and a-half as great as in the five years from 1845 to 1850.

Our Librarian, Mr. Watts, whose appointment was announced at the last Anniversary Meeting, has prepared a new Catalogue of the Society's Books. The Council is indebted to him for the promptitude and care with which he has produced this work, which, it is hoped, will tend materially to enhance the usefulness of the library.

The last year has happily not been marked by the loss of any eminent Chemist, either among the Fellows or Foreign Members. We have, however, to record the death of three of our Fellows, Mr. Charles Cowper, Mr. J. Macfarlane, and Mr. David Oldfield. A brief notice of two of these gentlemen will not be out of place.

Mr. J. F. Macfarlane had attained the Diploma of the Royal College of Surgeons of Edinburgh, and in early life practised for a short period; but he soon devoted himself to the business of a manufacturing Chemist and Druggist, which he carried on in Edinburgh, where he acquired considerable reputation as a manufacturer of the alkaloids and of chloroform. In 1818, he entered the Royal Medical Society of Edinburgh; was elected one of its Presidents in 1822, and in 1850 had the distinction of Honorary Member conferred upon him. He also, during a period of forty years, took an active interest in public matters, and was engaged in many important movements for the political and social benefit of his fellow-citizens.

Charles Cowper, one of our original Members, died on the 23rd December, 1860; he was born in London, on the 8th August, 1821. He was the son of the late Professor Cowper, of King's College, London (the Inventor of the printing machine now in common use) and brother of Mr. E. A. Cowper, Civil Engineer. Mr. C. Cowper studied Chemistry from early youth, under Dr. Faraday, Mr. Brande, and more practically under Mr. William Maughan; he was engaged as Practical Chemist with Messrs. Chance & Co., the large Glass Manufacturers, of Smethwick, near Birmingham, at whose works he made several useful improvements in the mixtures for coloured glass best adapted for Horticultural purposes, and in the working of sulphuric acid chambers, &c. He commenced business on his own account in London, as a Patent Agent, in 1848, and having had continual opportunities of observing and studying Engineering, he soon established a considerable reputation as a Patent Agent, both as regarded Chemical and Mechanical Inventions; and, owing to his careful attention to his profession, no Patent that he had specified, was ever lost.

He was much respected by a wide circle of friends, for his uprightness of character and great moral worth, added to a very amiable disposition.

List of Papers read at the Meetings of the Chemical Society, from March, 1860, to March, 1861:—

1. "On the Artificial Production of Tartaric Acid:" by Messrs. Perkin and Duppa.
2. "On Crystallized Potassium and Sodium:" by Mr. C. E. Long.
3. "On the History of Cinnamic Acid:" by Mr. D. Howard.
4. "On the Action of Sodium on Iodide of Methyl:" by Messrs. Wanklyn and Buckheisen.
5. "On Zinc-methyl:" by Mr. J. A. Wanklyn.
6. "On the Stibethyls and Stibmethyls:" by Mr. G. B. Buckton.
7. "On some Derivatives of the Olefines:" by Dr. Guthrie.
8. "On Baudrimont's Protosulphide of Carbon:" by Dr. Lyon Playfair.
9. "On the Composition of Hydrated Acids of constant boiling point:" by Dr. H. E. Roscoe.
10. "On Acetoxybenzamic Acid, an Isomer of Hippuric Acid:" by G. C. Foster, Esq.
11. "On the discrepancies in the statements of Pelouze and F. Mohr, respecting the solubility of Gallotannic Acid in Ether:" by Professor Bolley.
12. "On a hitherto unobserved source of Paraffin:" by Professor Bolley.

13. "On the Crystalline form of Metallic Chromium:" by Professor Bolley.
14. "On the Colouring Matter of Persian Berries:" by Professor Bolley.
15. "On the Basic Carbonates of Copper:" by Mr. F. Field.
16. "On the Separation of Volatile Ethyl-alkaloids:" by Dr. Hofmann.
17. "On a new Lead-salt corresponding to Cobalt-yellow:" by Mr. S. D. Hayes.
18. "On the production of mixed Amines, Phosphines, and Arsines:" by Dr. Hofmann.
19. "On the Laws of Gas-absorption:" by Mr. J. H. Sims.
20. "On Sugar in Urine:" by Dr. H. Bence Jones.
21. "On the Separation of Tellurium from Selenium and Sulphur:" by Dr. Oppenheim.
22. "On Nitroprusside of Sodium as a Re-agent:" by Dr. Oppenheim.
23. "Analysis of the Saline-water of Purton, near Swindon:" by Dr. Noad.
24. "On the Composition of Purton Water:" by Dr. Voelker.
25. "On the Electrolytic test for Arsenic:" by Professor Bloxam.
26. "On a new Silver-phosphonium-compound:" by Dr. Hofmann.
27. "On the Carbonates of Copper, Cobalt, and Nickel:" by Mr. F. Field.
28. "On the Oxidation of Benzol:" by Mr. A. H. Church.
29. "On the Action of Dilute Nitric Acid upon some Hydrocarbons of the Benzol series:" by Drs. De la Rue and Müller.
30. "On the Putrefaction of Bile and Formation of Gall-stones:" by Dr. Thudichum.
31. "On the Bisulphide of Iodine:" by Dr. Guthrie.
32. "On Ground Ice:" by Mr. R. Adie.
33. "On some Minerals from Chile:" by Mr. F. Field.

List of Discources delivered at the Meetings of the Chemical Society:—

"On Ozone:" by Dr. Thomas Andrews.

"On Circular Polarization:" by Dr J. H. Gladstone.

"On Organo-metallic Bodies:" by Dr. Frankland.

"On Thermo-dynamics in relation to Chemical Affinity:" by Dr. Williamson.

The following Report of the financial state of the the Society was read by the Treasurer:—

Dr. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON. Cr.

1860.		£	s.	d.	£	s.	d.
March 26.	To Cash in hand				565	3	3
July.	,, Half-yearly Dividend on £450 3 per cent. Consols				6	9	5
1861.							
January.	,, Half-yearly Dividend on £500 3 per cent. ,,				7	3	9
	,, Sundry Receipts from 25th March, 1860, to 25th March, 1861, as below:—						
	Life Compositions	70	0	0			
	Admission Fees	42	0	0			
	Resident Members' Subscriptions previous to 1860	20	0	0			
	Non-resident Members' Subscriptions previous to 1860	10	0	0			
	Resident Members' Subscriptions for 1860	60	0	0			
	Non-resident Members' Subscriptions for 1860	37	0	0			
	Resident Members' Subscriptions for 1861	234	0	0			
	Non-Resident Members' Subscriptions for 1861	96	0	0	569	0	0
					£1147	16	5

1860.		£	s.	d.	£	s.	d.
Journal.	By Editor's Salary to 25th March, 1860				18	15	0
	,, ,, 25th ,, 1861				75	0	0
	,, Editorial Expenses				1	6	0
	,, Printing Journal				199	2	2
					294	3	2
	,, Proceedings of Royal Society				..	..	..
Library.	,, Librarian's Salary to 25th March, 1860				6	5	0
	,, ,, ,, ,, 1861				25	0	0
	,, Books and Magazines				6	7	0
	,, Bookbinding				30	11	8
	,, Spectrum Chart				0	5	0
	,, Subscription to Cavendish Society				1	1	0
					69	9	8
Collector and Clerk.	,, Collector's Commission				28	9	0
	,, Clerk				3	0	0
					31	9	0
	General Printing, Stationery, and Postages:—						
	By Harrison and Co.'s Account from July, 1858				29	17	6
	,, Other Accounts, &c.				12	5	9
	,, Carriage of Books, Postages, &c. (Hux's Book)				2	18	6
					45	1	9
	Attendance, Coals, Gas, &c.:—						
	By T. Hux, Attendance from Michaelmas, 1860, to 1861				20	0	0
	,, ,, (as per Book) Coals and Wood				1	8	0
	,, ,, ,, Gas and Oil				2	6	9
	,, Mr. and Mrs. Page, Lighting Fires				3	3	0
	,, Gate Porter				1	1	0
					27	18	9
	,, Royal Society, Share of Expenses for Refreshments				..	..	..
					17	4	6
					505	6	10
Furniture.	,, Book Case (T. Fox)				24	10	0
	,, Furniture (Hux's Book)				1	9	0
					25	19	0
June 26.	By Purchase of £50 3 per cent. Consols				..	..	..
					46	18	9
					578	4	7
	,, Balance at Coutts'				517	14	2
	,, ,, in Cash				51	17	8
					569	11	10
				£	1147	16	5

Assets	£	s.	d.
Balance in Cash	569	11	10
Invested in 3 per Cent. Consols	500	0	0
	£1069	11	10

Examined and found correct,
AUGUSTUS MATTHIESSEN,
CHARLES HEISCH,
DANIEL HANBURY,
} *Auditors.*

London, 26th March, 1861.

The following gentlemen were elected as Council and Officers for the ensuing year:—

President.—Dr. A. W. Hofmann.

Vice-Presidents who have filled the office of President.—W. T. Brande, B. C. Brodie, Dr. C. G. B. Daubeny, Thomas Graham, Dr. A. W. Miller, Dr. Lyon Playfair, Col. Philip Yorke.

Vice-Presidents.—Dr. H. Bence Jones, Robert Porrett, Alfred Smee, Dr. A. W. Williamson.

Secretaries.—T. Redwood, W. Odling.

Foreign Secretary.—Dr. E. Frankland.

Treasurer.—Dr. Warren De la Rue.

Other Members of Council.—Dr. Thomas Andrews, Dr. William Francis, Dr. J. H. Gladstone, Dr. G. D. Longstaff, Dr. Marcet, Dr. Normandy, W. H. Perkin, Dr. H. E. Roscoe, Dr. Edward Schunck, Dr. John Stenhouse, Robert Warington.

The thanks of the meeting were voted to the President, Officers, and Council, for their services to the Society; also to the Auditors and to the Scrutators.

April 4th, 1861.

Robert Warington, Esq., in the chair.

The following were elected Fellows of the Society:—

Frederick Norrington, Esq., 9, Charles-place, Plymouth; Robert Collyer, Ph.D., 8, Alpha-road, Regent's-park; Thomas Wood, Ph.D., 123, Upper Thames-street; Rev. John Henn, B.A., Greenhays, Manchester.

The following was elected an Associate of the Society:—

Mr. John Hall Smith, St. Mary's Hospital.

The following paper was read:—

"On some Derivatives from the Olefines:" by Dr. Frederick Guthrie.

April 18th, 1861.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society:—

DANIEL HANBURY, London, 26th March, 1861.

Balance in Cash 369 11 10
Invested in 3 per Cent. Consols 500 0 0
£1069 11 10

Henry K. Bamber, Esq., Cheyne-walk, Chelsea; Arthur Ernest Sansom, M.B., 70, Brook-street, and Park-lodge, Fulham.

By a vote of the meeting, passed in accordance with the Bye-laws, the following names were removed from the list of Fellows:—

A. G. Anderson, Benjamin Cooper, C. F. O. Glassford, C. R. James, J. E. Mayer, J. W. Perkins, Professor Pohl, Professor John Wilson.

Mr. Abel delivered a discourse—"On the Application of Electricity to the Explosion of Gunpowder."

May 2nd, 1861.

Robert Warington, Esq., in the chair.

Thomas Griffiths, Esq., 6, Stonefield-street, Lonsdale-square, N., was elected a Fellow of the Society:—

The following papers were read:—

"On the Action of Dibromide of Ethylene on Pyridine:" by Mr. J. Davidson.

"On the amount of Water displaced from the Hydrates of Potash, Soda, and Baryta, by Boracic and Silicic Acids:" by Professor Bloxam.

"On the Graphite of Cast-iron:" by Professor Crace Calvert.

May 16th, 1861.

Dr. Hofmann, President, in the chair.

The following were elected Fellows of the Society:—

Joseph Prestwich, Esq., F.R.S., Regent's-park; Thomas Lindsay, Esq., Millbank Brewery, Millwall; Edward Arnold, Esq., Norwich; Edward Cort Wright, Esq., 46, Mosley-street, Manchester.

Mr. W. H. Perkin delivered a discourse—"On the Colouring Matters obtained from Coal-tar."

June 6th, 1861.

Dr. Hofmann, President, in the chair.

The following papers were read:—

"On Bromide of Carbon:" by Mr. A. E. W. Lennox.

"On the power ascribed to the Roots of Plants of rejecting Poisons, or other Abnormal Substances presented to them:" by Dr. Daubeny.

June 20th, 1861.

Dr. Warren De La Rue, Treasurer, in the chair.

The following were elected Fellows of the Society:—

Dr. John Dauglish, Reading; Henry Curwen Salmon, F.G.S., 36, Lemon-street, Truro; W. H. Harris, Esq., 33, Gold-street, Northampton.

The following paper was read:—

"On the Constitution of Gastric Juice:" by Dr. Marcet.

A discourse was delivered by Dr. H. E. Roscoe—"On the Application of the Induction-coil to Steinheil's Apparatus for Spectrum analysis."

November 7th, 1861.

Dr. Hofmann, President, in the chair.

The following papers were read:—

"On the Action of certain Gases upon the Peroxides of Potassium and Sodium:" by A. Vernon Harcourt, Esq.

"On some results of the Analyses of Commercial Copper:" by Messrs. Abel and Field.

"On the occurrence of Bismuth in various descriptions of Copper ore:" by Mr. F. Field.

November 21st, 1861.

Dr. Hofmann, President, in the chair.

Peter McOwen, B.A., Huddersfield College, was elected a Fellow of the Society.

The following papers were read:—

"On Leucic Acid and some of its Salts:" by Dr. Thudichum.

"On the occurrence of Crystalline Deposits of Phosphate of Lime in human Urine:" by Dr. H. Bence Jones.

"On Sparteine:" by Mr. E. J. Mills.

December 5th, 1861.

Dr. Miller, Vice-President, in the chair.

The following papers were read:—

"On Peppermint-camphor:" by Dr. Oppenheim.

"On Piperic and Hydro-piperic Acids:" by G. C. Foster, B.A.

"On Supplementary Experiments upon the power ascribed to the Roots of Plants of rejecting Poisons and Abnormal Substances presented to them:" by Dr. Daubeny.

"On some Physical Properties of Tin-lead Alloys:" by Professor Bolley.

"On the Dangers arising from the use of certain Waters for feeding Steam-boilers:" by Professor Bolley.

Donations to the library received in the year 1861:—

"On Coal, Petroleum, and other distilled Oils;" by A. Gessner: from the Author.

"On the Origin of Species by means of Organic Affinity;" by H. Freke: from the Author.

"Memorials of Dr. Priestley;" by James Yates: from the Author.

"Report of Experiments on the Growth of Red Clover;" by J. B. Lawes, F.R.S., and J. H. Gilbert, Ph. D., F.R.S.: from the Authors.

"On the Sources of the Nitrogen of Vegetation;" by J. B. Lawes, F.R.S., J. H. Gilbert, Ph.D., F.R.S., and Evan Pugh, Ph.D., F.C.S.: from the Authors.

"On the Solubility of Bone-earth from various Sources in

Solutions of Chloride of Ammonium and Common Salt;" by James Birney: from the Author.

"Composition of Linseed and Rape Cakes, which are now selling (1859) in the Dublin Market; and the Composition of Artificial Cattle-food;" by James Birney and John McDowell: from the Authors.

"On the Separation of Copper and Iron by means of Ammonia, and the Analysis of some Irish Copper Ores;" by Edward Byrne: from the Author.

"On the Valuation of Soils and the Nutrition of Plants;" by Robert Galloway: from the Author.

"Investigations conducted at the Laboratory of the Museum of Irish Industry," (1858 to 1859): from the Directors.

"A Notice of the Origin, Progress, and Present Condition of the Academy of Natural Sciences of Philadelphia," (1860): by W. S. W. Raschenberger, M.D.: from the Academy.

"Contributions to the History of the Phosphorus-bases;" by A. W. Hofmann, Ph.D., F.R.S.: from the Author.

"On the Relation between Boiling Point and Composition in Organic Compounds;" by Dr. H. Kopp: from the Author.

"On the Conductibility of Mercury and Amalgams;" by Messrs. Calvert and Johnson: from the Authors.

"On the Expansion of Metals and Alloys;" by Messrs. Calvert and Johnson: from the Authors.

"Manual of Chemistry; Descriptive, Theoretical, and Practical;" by William Odling, M.B., F.R.S.: from the Author.

"Report on the Explosion of Gunpowder by Electricity;" by Messrs. Wheatstone and Abel: from the War Office.

"On the Chromate of Chromium and Analogous Chromates;" by F. H. Storer and C. W. Elliot: from the Authors.

On the Constitution of Anthracene or Paranaphthalin;" by T. Anderson: from the Author.

"Second Report of a Geological Reconnaissance of the Southern and Middle Counties of Arkansas:" from the Smithsonian Institution at Washington.

"Review of Dr. Antisell's Work on Photogenic Oils;" by F. H. Storer: from the Author.

"Traité de Chimie Générale Elémentaire;" par A. Cahours, 2me Edition, 3 tomes: from the Author.

"Histoire des Radicaux Organiques;" par A. Cahours: from the Author.

"Dictionnaire de Chimie Industrielle;" par MM. Barreswil et Girard, Introduction et Tome premier: from the Authors.

"Sur quelques Phenomènes Météorologiques sur le litoral de la Flandre occidentale," par T. L. Phipson.

"Sur une nouvelle Roche de formation recente sur le litoral de la Flandre occidentale," par T. L. Phipson.

"La Force catalytique, ou Etudes sur les Phenomènes de Contact," par T. L. Phipson.

"Sur une Matière colorante extracte du *Rhamnus Frangula*," par T. L. Phipson.

"Sur les Bolets bleuissants; Etudes de formation des Principes colorants chez plusieurs Champignons," par T. L. Phipson.

"Mémoire sur la Fécule et les substances qui peuvent la remplacer dans l'Industrie," par T. L. Phipson.

"Recherches nouvelles sur le Phosphore," par T. L. Phipson.

"Sur la Phosphorescence en générale, et sur les Insectes phosphoriques en particulier," par T. L. Phipson:

from the Author.

"Handbuch der technisch-chemischen Untersuchungen," von Dr. P. A. Bolley: from the Author.

"Ueber königliche Massnahmen für das Gedeihen der Wissenschaften," von F. von Thiersch: from the Royal Bavarian Academy of Sciences.

"Das chemische Laboratorium der Universität Christiania, und die darin ausgeführten chemischen Untersuchungen;" herausgegeben, von Adolph Strecker, Director des Laboratoriums: from the University of Norway.

Periodicals:—

"Philosophical Transactions," 1860, Pt. I.: from the Royal Society.

"Transactions of the Royal Society of Edinburgh," Vol. XXII., Pt. II.

"Appendix to the Makerstoun Magnetical and Meteorological Observations," being a Supplement to Vol. XXII of the Transactions of the Royal Society of Edinburgh.

"Proceedings of the Royal Society of Edinburgh," Session 1859 to 1860: from the Royal Society of Edinburgh.

"Memoirs of the Royal Astronomical Society," Vol. XXIX.

"Monthly Notices of the Royal Astronomical Society," from Dec. 1860, to Dec. 1861: from the Society.

"Quarterly Journal of the Geological Society for 1861:" from the Society.

"Notices of the Proceedings of the Members of the Royal Institution of Great Britain," Part 11 (1860–61).

"List of Members, Officers, &c., of the Royal Institution," 1861.

"Additions to the Library of the Royal Institution," from July 1860 to July 1861:

From the Royal Institution.

"Journal of the Photographic Society," for 1861: from the Society.

"Pharmaceutical Journal," for 1861: from the Editor.

"Journal of the Society of Arts," No. 422 to 472: from the Society.

"Chemical News," No. 55 to 69: from the Editor.

"Literary Gazette," No. 130 to 176: from the Editor.

"London Review," No. 31 to 73: from the Editor.

"The British Journal Photographic Almanac," for 1861: from the Editor.

"Calendar for the year 1861, of the Science and Art Department of the Committee of Council on Education:" from the Department.

"Twenty-eighth Report of the Royal Cornwall Polytechnic Society:" from the Society.

"Annual Report of the Yorkshire Philosophical Society," 1860: from the Society.

"Proceedings of the Royal Society of Liverpool" (1860–61): from the Society.

"Smithsonian Contributions to Knowledge," Vols. XI, XII.

"Smithsonian Reports," for 1859:

from the Smithsonian Institution at Washington.

"American Journal of Science and Arts," for 1861: from the Editor.

"Journal of the Franklin Institute," for 1861: from the Institute.

"Proceedings of the Academy of Natural Sciences of Philadelphia," for 1860, pp. 285 to 579, 1861, No. 1—4: from the Academy.

"Proceedings of the American Philosophical Society," Vol. VII, No. 63: from the Society.

"Annual Report of the Cooper Union of Sciences and Art," for 1860: from the Union.

"Canadian Journal:" from the Canadian Institute.

"Canadian Naturalist and Geologist," Vol. VI, No. 1—to 4: from the Natural History Society of Montreal.

"Bulletin de la Société d'Encouragement pour l'Industrie Nationale," No. 94—105: from the Society.

"Bulletin de la Classe des Sciences de l'Académie Royale de Belgique," 1860.

"Annuaire de l'Académie Royale de Belgique, 1861: from the Academy.

"Mélanges Physiques et Chimiques," Tome IV., Livraisons 1—5: from the Imperial Academy of Sciences at St. Petersburgh.

"Denkschriften der kaiserlichen Akademie der Wissenschaften zu Wien:" Band XIX.

"Sitzungsberichte der kaiserlichen Akademie der Wissenschaften zu Wien:" Band XLI, Nos. 13—20; Band XLII, Nos. 21—28; Band XLIII, 1.

"Jahrbuch der konigl.-kaiserlichen Central-Anstalt für Meteorologie and Erdmagnetismus," von Karl Kreil, 1855: from the Imperial Academy of Sciences at Vienna.

"Sitzungsberichte der königlich-baeyerischen Akademie der Wissenschaften zu München," 1860, Hefte 4—5; 1861. Hefte 1—4: from the Royal Bavarian Academy.

INDEX.

A.

Abel, F. A., account of recent researches on the application of electricity, from different sources, to the explosion of gunpowder, 165.

—— F. A., and F. Field: some results of the analysis of commercial coppers, 290.

Abel's fuzes for firing gunpowder with magneto-electric apparatus, 185.

Acetate of lead, action of basic and neutral, on solutions of sugar, 29.

Acid arsenious, effect of, in the soil, on the growth of barley and turnips, 223, 330.

—— benzoic, on a new homologue of, by A. H. Church, 52.

—— boracic, action of, upon hydrate of baryta at a red heat, 147.

—— boracic, action of, on hydrate of potash at a red heat, 144.

—— boracic, action of, on hydrate of soda at a red heat, 147.

—— carbonic, its action on binoxide of sodium, 284.

—— —— tetroxide of potassium, 285.

—— chloroxynaphthalic, 246.

—— collidinic, 56.

—— leucic, on, and some of its salts, by J. L. W. Thudichum, 307.

—— perchloroxynaphthalic, 247.

—— picric, dyeing of silk with, 250.

—— picric, or trinitrophenic, 243.

—— rosolic, 244.

—— salylic, 56.

—— silicic, action of, upon hydrate of baryta at a red heat, 150.

—— silicic, action of, upon hydrate of potash at a red heat, 149.

—— silicic, action of, upon hydrate of soda at a red heat, 150.

—— sulphurous, absorption of, in water, 2.

Acid, sulphurous, determination of its tension, 15.

—— terephthalic, 57.

—— trinitrophenic or picric, 243.

Adie, R., on the ice found under the surface of the water in rivers, called "Ground-ice," 111.

Adie's paper on "Ground-ice," note on, by E. Frankland, 113.

Alcohol process, Brücke's, detection of sugar in healthy urine, by, 36.

Algodonite, 161.

Alisonite, 160.

Alumina in *Lycopodiaceæ*, 222.

Ammonia in water, solubility of, 17.

—— its action on bromide of bromethyltriethylphosphonium, 325.

—— leucate of, 310.

Amylene, action of pentachloride of phosphorus on, 136.

—— bicyanide of, 137.

—— bisulphochloride of, 129.

—— bithio-bithiocyanide of, 134.

—— bithiocyanide of, 133.

—— group of phosphorus bases, 341.

Aniline, preparation of, from coal-tar, 231.

—— preparation of fuchsine by the action of bichloride of tin on, 237.

—— preparation of fuchsine by the action of mercurous nitrate on, 238.

—— green, or emeraldine, 241.

—— green, method of applying to fabrics, 253.

—— purple, dyeing of silk with, 250.

—— purple, dyeing of wool with, 251.

—— purple, preparation of, 232.

—— purple, properties of, 234.

Anniversary Meeting of the Chemical Society, (March 30th, 1861), 349.

Antimony, estimation of in commercial copper, 293.

—— and arsenic, detection of minute traces of, in copper, 295.

Armstrong's hydro-electric machine, use of, for exploding gunpowder, 176.
Arsammonium compounds, 355
Arsenic, detection of minute quantities of, in copper, 295.
—— estimation of, in commercial copper, 293.
Artificial light: its effect on coal-tar colours, 254.
Azobenzol and benzidine, on, by P. W. Hofmann, 60.
Azuline, 249.
—— dycing of silk with, 251.

B.

Balance sheet of the Chemical Society, 1861, 352.
Barley, effect of arsenious acid in the soil, on the growth of, 223.
—— and turnips, effect of baryta and strontia in the soil, on, 227.
Baryta, action of boracic acid on hydrate of, at a red heat, 147.
—— action of silicic acid upon hydrate of, at a red heat, 150.
—— and strontia in the soil, effect of, on barley and turnips, 227.
—— leucate of, 310.
Basic carbonates of copper, on the, by F. Field, 70.
—— persulphate of iron, from Chile, 156.
Benzylene, dichloride of: its action on triethylphosphine, 343.
—— group of phosphorus bases, 3yl.
Benzidine, diethylated and tetrethated, 63.
—— on azobenzol and, by P. W. Hofmann, 60.
Benzol-series, on some products of the action of dilute nitric acid on some hydrocarbons of the, by Warren De la Rue and Hugo Müller, 54.
Bichloride of tin, preparation of fuchsine by the action of, on aniline, 237.
Bicyanide of amylene, 137.
Bile, diagram exhibiting the decomposition of, 120.
—— human, putrefaction and analysis of, 127.
—— ox, analysis of putrid, 126.
—— putrefaction of, 118.
Bismuth, detection of, in copper, 299.
—— estimation of, in commercial copper, 294.
—— in copper coinage, 300.
Bismuth, on the general distribution of, in copper minerals, by F. Field, 304.
Binoxide of sodium, action of carbonic acid on, 284.
—— action of carbonic oxide on, 283.
—— action of nitric oxide on, 287.
—— action of protoxide of nitrogen on, 285.
—— hydrate of, 279.
—— its analysis, 277.
—— preparation, 276.
Bisulphide of iodine, on the, by F. Guthrie, 57.
Bisulphochloride of amylene, 129.
—— ethylene, 129.
Bithio-bithiocyanide of amylene, 134.
Bithiocyanide of amylene, 133.
Bleu de Paris, 241.
Bloxam, C. L., on the amount of water displaced from the hydrates of potash, soda and baryta, by boracic and silicic acids, 143.
Blue, chinoline, 246.
—— of Paris, 241.
Boron, carbon, and silicon, atomic weights of, 153.
Bournonite from Chile, 158.
Bromethyl-triethylarsonium, compound of, 336.
—— triethylphosphonium, action of ammonia, on bromide of, 325.
—— action of dimethylamine and trimethylamine, on bromide of, 331.
—— action of ethylamine, on bromide of, 328.
—— action of methylamine on bromide of, 328.
—— action of triethylarsine, on bromide of, 333.
—— bromide of, 78, 320.
—— gold-salt of, 82.
—— platinum-salt of, 80, 321.
—— salts of, 78.
Bromide of bromethyl-triethylarsonium, 336.
—— triethylphosphonium, 78, 320.
—— of cajputene, 68.
—— of carbon, on the, by A. E. W. Lennox, 205.
—— of oxethyl-triethylphosphonium, 84.
—— of silver with dibromide of ethylene-benethyl diphosphonium, 102.
Brücke's processes for the detection of sugar in urine, 32, 36.

C:

Cajeput, on the constitution of oil of, by M. Schmidl, 63.
Cajputene, 64.
—— bihydrate of, 66.
—— bromide of, 68.
—— chloride of, 67.
—— hexhydrate of, 67.
—— hydrates of, 65.
—— hydriodate of, 69.
—— hydrochlorates of, 68.
—— monohydrate of, 65.
Calico-printing, with coal-tar colours, 252.
Calvert, F. C., on the composition of a carbonaceous substance existing in grey cast iron, 199.
Carbon, on the bromide of, by A. E. W. Lennox, 205.
—— boron, and silicon, atomic weights of, 153.
Carbonate of ethylene-hexethyl-diphosphonium, 99.
—— of soda: its action on decarbonate of copper, 71.
Carbonates of copper, on the, with some remarks on the carbonates of nickel and cobalt, 48.
—— of copper, on the basic, by F. Field, 70.
Carbonic acid: its action on binoxide of sodium, 284.
—— tetroxide of potassium, 285.
—— oxide: its action on binoxide of sodium, 283.
Carminaphtha, 247.
Cast iron, on the composition of a carbonaceous substance existing in grey, by F. C. Calvert, 199.
Chemical Society, anniversary meeting, (March 30, 1861,) 349.
—— balance sheet, 1861, 352.
—— donations to the Library, (1861), 356.
—— proceedings at the meetings, 347.
—— report of the President and Council, (1861), 347.
Chile, on some minerals from, by F. Field, 153.
Chinoline colours, dyeing of silk with, 250.
—— dyeing of wool with, 251.
—— or quinoline, colouring matters of, 245.
Chlorethylated triethylphosphonium, platinum salt of, 317.
Chloride of cajputene, 67.
—— of oxethyl-triethylphosphonium, 34.
—— of vinyl-triethylarsonium, 337.
Chlorine, action of, on solutions of sugar, 31.
Chromate of ethylene-hexethyl-diphosphonium, 99.
Church, A. H., preliminary note concerning a new homologue of benzoic acid, 52.
Coal-tar, on colouring matters derived from, by W. H. Perkin, 230.
Coal-tar colours, how affected by artificial light, 253.
—— method of dyeing cotton with, 251.
—— printing calico with, 252.
—— spectra produced by, 254.
—— their application to the arts of dyeing silk and wool, 250.
—— their preparation not injurious to workmen, 255.
Cobalt, carbonates of, 49.
—— leucate of, 310.
Colouring matters of quinoline or chinoline, 244.
—— on, derived from coal-tar, by W. H. Perkin, 230.
Colours, application of coal-tar, to the dyeing of silk and wool, 250.
—— from naphthaline, 246.
Copper, action of carbonate of soda on dicarbonate of, 71.
—— and lead, double sulphide of, from Chile, 160.
—— coinage, presence of bismuth in, 300.
—— minerals, on the general distribution of bismuth in, by F. Field, 304.
—— on the basic carbonates of, by F. Field, 70.
—— on the carbonates of, with some remarks on the carbonates of nickel and cobalt, by F. Field, 48.
—— protoxide of, from Chile, 154.
—— qualitative and quantitative examination of, containing antimony, arsenic, bismuth, and lead, 291.
—— subphosphide of: its use as a primary composition for igniting gunpowder by electricity, 184.
—— table showing the results of the examination for metallic impurities, of different varieties of, 301.
Coppers, some results of the analysis of commercial, by F. A. Abel and F. Field, 290.
Cotton, method of dyeing with coal-tar colours, 251.
Cuproplumbite from Chile, 108.
Cowper, Charles, obituary notice of, 350.

D.

Darwinite, 161.
Daubeny, C., on the power ascribed to the roots of plants, of rejecting poisonous or abnormal substances presented to them, 209.
Davidson, John, on the action of dibromide of ethylene on pyridine, 161.
De La Rue, Warren, and Hugo Müller, on some products of the action of dilute nitric acid on some hydrocarbons of the benzol series, 54.
Diarsonium compounds, 338.
Dibromide of dibrominated ethylene, 206.
—— of ethylene: its action on triethylarsine and triethylatibine, 335, 341.
—— its action on triethylphosphine, 76.
—— its action on trimethylphosphine, 320.
—— on the action of, on pyridine, by John Davidson, 161.
—— dipyridyl-diarsonium, 163.
—— hexethyl-diarsonium, 338.
—— hexethyl-diphosphonium, 95.
—— hexmethyl-diphosphonium, 323.
—— triethylarsammonium, 339.
—— of tribrominated ethylene, 208.
Dichloride of benzylene: its action on triethylphosphine, 343.
—— of ethylene: its action on triethylphosphine, 316.
—— dipyridyl-diammonium, 163.
—— hexethyl-diphosphonium, 35.
—— of triethyl-benzylphosphonium, 343.
Dicyanide of ethylene-hexethyl-diphosphonium, 98.
Dicarbonate of copper, action of carbonate of soda on, 71.
Diethylamine: its action on bromide of bromethyl-triethylphosphonium, 331.
Difluoride of ethylene-hexethyl-diphosphonium, 98.
Dihydrate of ethylene.hexethyl-diphosphonium, 92.
—— phospharsonium, 333.
Di-iodate of ethylene-hexethyl-diphosphonium, 99.
—— of ethylene: its action on triethylphosphine, 318.
—— hexethyl-phosphonium with iodide of zinc, 102.
—— diphosphonium, 95.
—— hexmethyl-diphosphonium, 324.
—— tetrethyl-phosphammonium, 330.
Dinitraniline, 242.
Dinitrate of ethylene-hexethyl-diphosphonium, 99.
Diphosphonium compounds, 89.
Diperchlorate of ethylene-hexethyl-diphosphonium, 99.
Dipicrate of ethylene-hexethyl-diphosphonium. 100,
Disulphydrate of ethylene-hexethyl-diphosphonium, 95.
Disulphocyanate of ethylene-hexethyl-diphosphonium, 99.
Domeykite, 161.
Donations to the Library of the Chemical Society in 1861, 356.
Duckweed, ash of, 219.
Dyeing silk and wool with coal-tar colours, 250.

E.

Electricity, account of recent researches on the application of, from different sources, to the explosion of gunpowder, by F. A. Abel, 165.
—— frictional, experiments on the explosion of gunpowder by, by F. A. Abel, 174.
Electro-magnetic induction apparatus, experiments on the explosion of gunpowder by, by F. A. Abel, 168.
Emeraldine, 241.
Ethylamine, its action on bromide of bromethyl-triethyl-phosphonium, 328.
Ethylene, action of dibromide on triethylarsine and triethyl-stibine, 335, 336.
—— action of dibromide of, on triethylphosphine, 76.
—— action of dibromide of, on trimethylphosphine, 320.
—— bisulphochloride of, 129.
—— dibromide of dibrominated, 206.
—— dichloride of, its action on triethylphosphine, 316.
—— on the action of dibromide of, on pyridine, by John Davidson, 161.
—— di-iodide of, its action on triethylphosphine, 318.
—— tribrominated, 207.
—— diethyl-phosphonium, hybrids of, 319.
—— dipyridyl-diammonium, 164.
—— group of diatomic phosphorus-bases, 76.
—— hexethyl-diarsonium, compounds of, 338.
—— hexethyl-diphosphonium, action of heat upon the hydrate of, 103.

Ethylene, hexethyl-phospharsonium, compounds of, 333.
—— methyl-triethyl-phosphammonium, 328.
—— pentethyl-phosphammonium, compounds of, 331.
—— tetrethylphammonium, compounds of, 328.
—— triethylarsammonium, compounds of, 339.
—— triethyl-phosphammonium, gold-salt of, 326.
—— —— platinum-salt of, 325.
—— trimethyl-triethyl-phosphammonium, compounds of, 333.
Ethylene-hexethyl-diphosphonium, argentobromide of, 102.
—— carbonate of, 89.
—— chromate of, 99.
—— dibromide of, 89.
—— dichloride of, 95.
—— dicyanide of, 98.
—— difluoride of, 98.
—— dihydrate of, 92.
—— di-iodate of, 99.
—— di-iodide of, 95.
—— dinitrate of, 99.
—— diperchlorate of, 99.
—— dipicrate of, 100.
—— disulphydrate of, 95.
—— disulphocyanate of, 99.
—— gold-salt of, 101.
—— mercury-salt of, 101.
—— oxalate of, 100.
—— palladium-salt of, 101.
—— phosphate, 100.
—— platinum-salt of, 100.
—— silicofluoride of, 98.
—— sulphate of, 99.
—— tartrate of, 100.
—— tin-salt of, 102.
—— zinc-iodide of, 102.

F.

Fabrics, method of applying aniline-green to, 253.
Fermentation, on the proof of the presence of sugar in healthy urine by, 39
—— of sugar, comparison of the delicacy of, and with Fehling's standard solution, 27.
—— test of sugar, 24.
Field, F., on some minerals from Chile, 153.
Field, F., on the basic carbonates of copper, 70.
—— on the basic carbonates of copper, with some remarks on the carbonates of nickel and cobalt, 48.
—— on the general distribution of bismuth in copper minerals, 304.
—— and F. A. Abel, some results of the analysis of commercial coppers, 290.
Frankland, E., note on Mr. Adie's paper on "Ground-ice," 113.
Frictional electricity, experiments on the explosion of gunpowder by, 174.
Fuchsine, or magenta, 237.
—— dyeing of silk with, 250.
—— dyeing of wool with, 251.
—— preparation of, by the action of bichloride of tin on aniline, 237.
—— preparation of, by the action of mercurous nitrate on aniline, 238.
—— properties of, 239.
Fuzes, Abel's, for firing gunpowder with magneto-electric apparatus, 182, 185.

G.

Gallstones, analysis of human, 121.
—— analysis of ox-, 123.
—— theory of, 116.
Gas-absorption, contribution to the knowledge of the laws of, by F. H. Sims, 1.
Gastric juice, researches on the constituents of, by W. Marcet, 256.
—— its optical rotatory power, 256
Gold-salt of bromethyl-triethylphosphonium, 82.
—— of ethylene-hexethyl-diarsonium, 338.
—— of ethylene-hexethyl-diphosphonium, 101.
—— of ethylene-tetrethyl-phosphammonium, 330.
—— of ethylene-triethylarsammonium, 339.
—— of ethylene-triethylphosphammonium, 326.
—— of oxethyl-triethylphosphonium, 85.
Graphitoidal substance in grey cast-iron, 203.
Green, aniline-, or emeraldine-, 241.
—— method of applying to fabrics, 253.
—— chimoline, 246.
Grey cast iron, on the composition of a carbonaceous substance existing in, by F. C. Calvert, 199.

Ground-ice, on, by R. Adie, 111.
—— note on Mr. Adie's paper on, by E. Frankland, 113.
Gunpowder, account of recent researches on the application of electricity, from different sources, to the explosion of, by F. A. Abel, 165.
Guthrie, F., on some derivatives from the olefines, 128.
———— on the bisulphide of iodine, 57.

H.

Harcourt, A. Vernon, on the peroxides of potassium and sodium, 267.
Heat, action of, upon the hydrate of ethylene-hexethyl-diphosphonium, 103.
—— effect of application of, to the roots of plants, 222.
Hofmann, A. W., Contributions to the history of the phosphorus-bases (Second Memoir), 73.
———— (Third Memoir), 316.
———— P. W., on azobenzol and benzidine, 60.
Human bile, putrefaction and analysis of, 127.
—— gall-stones, analysis of, 123.
Hybrids of ethylene-diethyl-phosphonium, 319.
Hydrate of baryta, action of boracic acid upon, at a red heat, 147.
—— —— action of silicic acid upon, at a red heat, 150.
—— of binoxide of sodium, 229.
Hydrates of cajputene, 65.
—— of ethylene-dipyridyl-diammonium, 164.
—— of ethylene-hexethyl-diphosphonium, action of heat upon the, 103.
—— of ethylene-hexethyl-diphosphonium, reactions of, 93.
—— of ethylene tetrethyl-phosphammonium, 330.
—— of oxethyl-triethylphosphonium, 84.
—— of potash, action of boracic acid on, at a red heat, 144.
—— —— action of silicic acid on, at a red heat, 149.
—— of soda, action of boracic acid on, at a red heat, 147.
—— —— action of silicic acid on, at a red heat, 150.
—— of vinylated triethylphosphonium, 327.
Hydriodate of cajputene, 69.
Hydrocarbons of the benzol-series, on some products of the action of dilute nitric acid on some, by Warren de la Rue and Hugo Müller, 54.
Hydrochlorates of cajputene, 68.
Hydro-electric machine, Armstrong's, use of, for exploding gunpowder, 176.

I.

Ice, on the, found under the surface of the water in rivers, called "Ground-ice," by R. Adie, 111.
Irisine, 232.
Iodide of oxethyl-triethylphosphonium, 83.
—— of tetrethyl-diphosphonium, crystalline form of, 109.
—— of zinc with di-iodide of ethylene-hexethyl-diphosphonium, 102.
Iodine, on the bisulphide of, by F. Guthrie, 57.
Iron, basic persulphate of, from Chile, 156.
—— grey cast, on the composition of a carbonaceous substance existing in, by F. C. Calvert, 199.
—— in carbonaceous substance existing in grey cast iron, 292.
Isocajputene, 64.

J.

Jones, H. Bence, on sugar in the urine, 22.
Juice, gastric: its optical rotatory power, 256.
—— —— researches on the constituents of, by W. Marcet, 256.

L.

Lead, action of basic and neutral acetate of, on solutions of sugar, 29.
—— and copper, double sulphide of, from Chile, 160.
—— black amorphous sulphate of, from Chile, 156.
—— estimation of, in commercial copper, 294.
—— leucate of, 315.
—— process, Brücke's, detection of sugar in healthy urine by, 37.

Lehmann's process for the detection of sugar in urine, 23.
Lemna trisulca, ash of, 219.
Lennox, A. E. W., on the bromide of carbon, 205.
Leucate of ammonia, 310.
—— of baryta, 310.
—— of cobalt, 310.
—— of lead, 315.
—— of lime, 310.
—— of magnesia, 310.
Leucates of mercury, 313.
Leucate of silver, 314.
—— of soda, 310.
—— of zinc, 311.
Library of the Chemical Society, Donations to, in 1861, 356.
Light, effect of artificial, on coal-tar colours, 254.
Lime, leucate of, 310,
Lycopodiaceæ, alumina in, 222.

M.

Macfarlane, J. F., obituary notice of, 349.
Magenta or fuchsine, 237.
Magnesia, leucate of, 310.
Magnets, permanent, experiments on the application of, to the explosion of gunpowder and to submarine operations, 180.
Marcet, W., researches on the constituents of gastric juice, 256.
Mauve dye, 232.
Meetings of the Chemical Society, proceedings at the, (1861), 317.
Mercurous nitrate, preparation of fuchsine by the action of, on aniline, 238.
Mercury, leucates of. 313.
—— salt of ethylene-hexethyl-diphosphonium, 101.
Methylamine: its action on bromethyltriethylphosphonium, 344.
Methylene-group of phosphorus-bases, 340.
Minerals, on some, from Chile, by F. Field, 153.
Monophosphonium compounds, 78.
Müller, Hugo, and Warren de la Rue, on some products of the action of dilute nitric acid on some hydro-carbons of the benzol series, 54.

N.

Naphthaline colours, 246.
Naphthamein, 248.
Nickel, carbonates of, 51.
Ninaphthlamine, 247.
Nitrazophenylamine, 243.
Nitric oxide: its action upon binoxide of sodium, 287.
—— —— its action upon tetroxide of potassium, 288.
Nitrogen in carbonaceous substance existing in grey cast iron, 201.
Nitrosonaphthalin, 247.
—— application of, to dyeing and printing, 253.
Nitrosophenylene-diamine, 242.
Nitrosophenyline, 242.
Nitroxamylene, nitroxisulphide of, 139.
Noad, H. M., analysis of the saline water of Purton, near Swindon, North Wilts, 43.

O.

Obituary notices of deceased fellows, 349.
Oil of cajeput, on the constitution of, by M. Schmidl, 63.
Olefines, on some derivatives from the, by F. Guthrie, 128.
Optical rotatory power of gastric juice, 256.
Oxalate of ethylene-hexethyl-diphosphonium, 100.
Ox-bile, analysis of putrid, 126.
Oxethyl-triethylphosphonium, bromide, chloride, hydrate, perchlorate, and platinum-salt of, 84.
—— —— gold-salt of, 85.
—— —— iodide of, 83.
—— trimethylphosphonium, compounds of, 314.
Ox-gallstones, analysis of, 123.

P.

Palladium-salt of ethylene-hexethyl-diphosphonium, 101.
Paracajputene, 65.
Paradiphosphonium compounds, 105.
Parapeptone, 260.
Peptone, 257.

Perkin, W. H, on colouring matters derived from coal tar, 230.
Perchlorate of oxethyl-triethylphosphonium, 84.
Peroxide of potassium: its analysis, 274.
—— its preparation, 268.
Peroxides of potassium and sodium, on the, by A. Vernon Harcourt, 267.
—— their behaviour with various reagents, 281.
Persulphate of iron, basic, from Chile, 156.
Pettenkofer's test for sugar, 31.
Phenamine, 232.
Phenylene-group of phosphorus-bases, 341.
Phosphammonium-compounds, 331.
Phospharsonium-compounds, 332.
Phosphate of ethylene-hexethyl-diphosphonium, 100.
Phosphide of copper fuze for firing gunpowder with magneto-electric apparatus, 185.
Phosphorus-bases, amylene-group of, 341.
—— contributions to the history of, (Second memoir): by A. W. Hofmann, 73.
—— Third Memoir, 316.
—— benzylene-group of, 358.
—— diatomic, 89.
—— diatomic, ethylene-group, 76.
—— diatomic, theory of, 73.
—— methylene-group of, 340.
—— monatomic, 78.
—— phenylene-group of, 341.
—— propylene-group of, 341.
—— series of mixed diatomic, 334.
Plants, effect of application of heat to the roots of, 222.
—— on the power ascribed to the roots of, of rejecting poisonous or abnormal substances presented to them: by C. Daubeny, 209, 330.
Platinum-salt of bromethyl-triethylarsonium, 336.
—— salt of bromethyl-triethyl-phosphonium, 80, 320.
—— salt of chlorethylated triethyl-phosphonium, 307.
—— salt of ethylene-dipyridyl-diammonium, 164.
—— salt of ethylene-hexethyl-diarsonium, 338.
—— salt of ethylene-hexethyl-diphosphonium, 100.
—— salt of ethylene-hexethyl-phospharsonium, 333.
—— salt of ethylene-hexethyl-diphosphonium, 324.
—— salt of ethylene-tetrethyl-phosphammonium, 328.
Platinum-salt of ethylene-triethyl-arsammonium, 339.
—— salt of tetrethyl-phosphonium, crystalline form of, 110.
—— salt of oxethyl-triethyl-phosphonium, 84.
—— salt of ethylene-triethyl-phosphammonium, 325.
—— salt of vinyl-triethyl-arsonium, 337.
Poisonous substances, on the power ascribed to the roots of plants of rejecting: by C. Daubeny, 209.
Potash, action of boracic acid on the hydrate of, at a red heat, 144.
—— action of silicic acid upon the hydrate of, at a red heat, 149.
—— and soda, proportions of, in plants grown under different circumstances, 215.
Potassium, action of carbonic acid on tetroxide of, 285.
—— action of carbonic oxide on tetroxide of, 284.
—— action of nitric oxide on tetroxide of, 288.
—— analysis of its peroxide, 274.
—— and sodium, on the peroxides of: by A. Vernon Harcourt, 267.
—— preparation of its peroxide, 268.
—— purification of, 269.
Printing calico with coal-tar colours, 252.
Proceedings at the meetings of the Chemical Society, (1861,) 317.
Propylene-group of phosphorus-bases, 341.
Protoxide of copper from Chile, 154.
Protoxide of nitrogen, its action on binoxide of sodium, 285.
Purple, aniline, 233.
Purton saline water, on the composition of: by A. Voelcker, 46.
—— analysis of: by H. M. Noad, 43.
Putrefaction and analysis of human bile, 127.
Putrefaction of bile, 118.
Putrid ox-bile, analysis of, 126.
Pyridine, on the action of dibromide of ethylene on: by John Davidson, 161.

Q.

Quinoline or chinoline, colouring matters of, 245.

R.

Red, magenta-, or fuchsine, 237.
Report of the President and Council of the Chemical Society (1861), 349.
Rheotome, 169.
Roots of plants, effect of the application of heat to, 222.
—— on the power ascribed to the, of rejecting poisonous or abnormal substances presented to them: by C. Daubeny, 209.
Roseine, 236.
—— dyeing of silk with, 250.
—— dyeing of wool with, 251.
Rotation observed in healthy urine, 39.
Rotatory power, optical, of gastric juice, 256.
Ruhmkorff's coil, ignition of gunpowder by, 169.

S.

Saccharimeter, Soleil's, 27.
Salm-Horstmar's experiments on the growth of plants, 212.
Schmidl, Maximilian, on the constitution of oil of cajeput, 63.
Silicates, formulæ of, 152.
Silicium in carbonaceous substance existing in, in grey cast iron, 202.
Silicofluoride of ethylene-hexethyl-diphosphonium, 98.
Silicon, boron and carbon, atomic weights of, 153.
Silk and wool, application of coal-tar colours to the dyeing of, 250.
Silk, dyeing of, with aniline purple, violine, and roseine, 250.
—— dyeing of, with azuline, 251.
—— dyeing of, with fuchsine, picric acid, chinoline blue, and chinoline violet, 250.
Silver, bromide of, with dibromide of ethylene-hexethyl-diphosphonium, 102.
—— leucate of, 314.
Sims, T. H., contributions to the knowledge of the laws of gas-absorption, 1.
Soda, action of boracic acid on hydrate of, at a red heat, 147.
—— action of silicic acid upon hydrate of, at a red heat, 150.
—— and potash, proportions of, in plants grown under different circumstances, 215.
—— leucate of, 310.
Sodium, action of carbonic acid on binoxide of, 284.
—— action of carbonic oxide on binoxide of, 283.
—— action of nitric oxide on binoxide of, 287.
—— action of protoxide of nitrogen on binoxide of, 285.
—— and potassium, on the peroxides of: by A. Vernon Harcourt, 267.
—— hydrate of binoxide of, 279.
—— oxidation of, 276.
—— peroxide of: its analysis, 277.
—— —— its preparation, 276.
Soleil's saccharimeter, 27.
Spectra of coal-tar colours, 254.
Strontia in the soil, effect of, on barley and turnips,
Sulphosphide of copper, use as a priming composition for igniting charges of gunpowder by electricity, 184.
Submarine charges, firing of, with magneto-electric apparatus, 193.
Sugar, action of basic and neutral acetate of lead on solutions of, 29.
—— action of chlorine on solutions of, 31.
—— detection of, in healthy urine by Brücke's alcohol process, 36.
—— detection of, when added to healthy urine, 22.
—— detection of, by Lehmann's process, 23.
—— detection of, in healthy urine by Brücke's lead process, 37.
—— on the detection of, naturally present in healthy urine, 35.
—— determination of the amount of, present in healthy urine, 40.
—— fermentation-test of, 24.
—— in the urine, on: by H. Bence Jones, 22.
—— in urine, Brücke's processes for the detection of, 32.
—— on the proof of the presence of, in healthy urine, by fermentation, 39.
—— Pettenkofer's test for, 31.
—— Trommer's test for, 32.
Sulphate of ethylene-hexethyl-diphosphonium, 19.
Sulphate of lead, black amorphous, from Chile, 156.
Sulphide of copper and lead, from Chile, 160.
Sulphurous acid: tables of solubility of in water at different pressures and temperatures, 11, 15.

T.

Tar red, 249.
Tartrate of ethylene-hexethyl-diphosphonium, 100.
Tetroxide of potassium, action of carbonic acid on, 285.
—— action of carbonic oxide on, 284.
Tension of sulphurous acid, determination of, 15.
Tetrethyl-diphosphonium, crystalline form of iodide of, 109.
Tetrethyl-diphosphonium, crystalline form of the platinum salt of, 110.
Thudichum, Dr., on the putrefaction of bile and the theory of gall-stones, 115.
———— on leucic acid and some of its salts, 307.
Tin, preparation of fuchsine by the action of bichloride of, on aniline, 237.
—— salt of ethylene-hexethyl-diphosphonium, 102.
Tetroxide of potassium, action of nitric oxide on, 288.
—— its analysis, 274.
—— its preparation, 268.
Tribrominated ethylene, 207.
Triethylarsine, action of dibromide of ethylene on, 336.
—— its action on bromide of bromethyl-triethylphosphonium, 333.
Triethyl-benzylphosphonium, chloride of, 343.
Triethylphosphine, action of dibromide of ethylene on, 76.
—— action of dichloride of ethylene on, 316.
—— action of di-iodide of ethylene on, 318.
—— its action on dichloride of benzylene, 343.
Triethylphosphonium, hydrate of vinylated, 327.
Triethylstibine, action of dibromide of ethylene on, 335.
Trimethylamine, its action on bromide of bromethyl-triethylphosphonium, 331.
Trimethylphosphine, action of dibromide of ethylene on, 320.
—— its action on bromide of bromethyl-triethylphosphonium, 319.
Trommer's test for sugar, 32.
Turnips, effect of arsenious acid in the soil in the growth of, 223.
—— effects of baryta and strontia on the growth of, 227.
Tyrian purple, 232.

U.

Urine, Brücke's processes for the detection of sugar in, 32.
—— detection of sugar in healthy, by Brücke's alcohol process, 36.
—— detection of sugar naturally present in healthy, 35.
—— detection of sugar when added to healthy, 22.
—— determination of the amount of sugar present in healthy, 40.
—— on sugar in; by H. Bence Jones, 22.
—— rotation observed in healthy, 39.

V.

Vinethyl-triethylphosphonium, salts of, 88.
Vinylated triethylphosphonium, hydrate of, 327.
Vinyl-triethylarsonium, compounds of, 337.
Violet, chinoline, 246.
Violine, 235.
—— dyeing of silk with, 250.
—— dyeing of wool with, 251.
Voelcker, A., on the composition of Purton saline water, 46.

W.

Wool, dyeing of, with aniline purple, violine, roscine, fuchsine, and chinoline colours, 251.
Wool and silk, application of coal-tar colours to the dyeing of, 250.
Water, absorption of sulphurous acid in, 2.
—— analysis of the saline, at Purton, near Swindon, North Wilts, by H. M. Noad, 43.
—— on the amount of, displaced from the hydrates of potash, soda, and baryta, by boracic and silicic acids: by C. L. Bloxam, 143.
—— on the composition of Purton saline: by A. Voelcker, 46.

Water, on the ice found beneath the surface of the, in rivers, called "ground ice": by R. Adie, 111.
—— solubility of ammonia in, 17.
—— tables of solubility of sulphurous acid in, at different pressures and temperatures, 11, 15.

Z.

Zinc, leucate of, 311.
—— iodide of, with di-iodide of ethylene hexethyl-diphosphonium, 102.

LONDON: PRINTED BY HARRISON AND SONS, ST. MARTIN'S LANE, W.C.